Quantum reactive scattering: the time - independent approach
II. Current methods and developments

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II.1 Introduction

II.2 Linear algebraic variational approach with Jacobi coordinates versus propagation methods with hyperspherical coordinates

Hulthén-Kohn variational principle

• oldest variational method for scattering problems: introduced by Hulthén (1944)

• four years later: Hulthén and Kohn developed independently the Hulthén-Kohn variational principle (**HKVP**)

• Rayleigh-Ritz method combined with boundary conditions for the scattering

• two other famous variational principles: Schwinger and Newton, where matrix elements with Green's functions are needed; these are more difficult to calculate and are collision energy dependent

• in the HKVP just matrix elements of the Hamilton operator are needed

- the problem of the HKVP: it is not invariant with respect to the choice of boundary conditions, leading to problems with pseudo resonances

- using stationary wave boundary conditions for the calculation of the K-matrix and calculation of the scattering matrix from the K-matrix with $S = (1 + iK)(1 - iK)^{-1}$ leads to different results as calculating the same S-matrix by using incoming and outgoing wave boundary conditions

- S-matrix version of the HKVP was developed by Miller and Jansen op de Haar

Variational principle for scattering

derivation of HKVP: potential scattering with $V(R)$, R: translational coordinate

radial SE ($\hbar$=1, m=1):

$$\left(\frac{d^2}{2dR^2} - \frac{l(l+1)}{R^2} - V(R) + k^2 \right) \Psi_l(R) = 0 \tag{1}$$

$$k^2 = E \tag{2}$$

$\Psi_l(R)$ is regular at the origin:

$$\Psi_l(0) = 0 \tag{3}$$

asymptotic form:

$$\Psi_l(R) \sim \sin(kR - \frac{l\pi}{2} + \eta_l) \tag{4}$$

η_l: exact phase-shift

functional defined as:

$$I_l = \int_0^\infty \tilde{\Psi}_l(R) L \tilde{\Psi}_l(R) dR \tag{5}$$

$$L = \left(\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} - V(R) + k^2 \right) \tag{6}$$

– trial wavefunction $\tilde{\Psi}_l(R)$ (approximation for the exact wavefunction $\Psi_l(\mathrm{R})$) (fulfills (3 and 4) with the chosen phase shift $\tilde{\eta}_l$

– the functional I_l is 0, if the Ansatz for $\tilde{\Psi}_l(R)$ is equal to the exact wavefunction $\Psi_l(R)$

– varying the wavefunction by $\delta\tilde{\Psi}_l(R)$ a new function is obtained

$$\tilde{\Psi}_l(R) = \Psi_l(R) + \delta\tilde{\Psi}_l(R) \tag{7}$$

$\delta\tilde{\Psi}_l(R)$ fulfils the boundary conditions:

$$\delta\tilde{\Psi}_l(R \to 0) = 0 \tag{8}$$

$$\lim_{R\to\infty} \delta\tilde{\Psi}_l(R) \sim \cos(kR - \frac{l\pi}{2} + \delta\tilde{\eta}_l) \tag{9}$$

with (7) in (5) one gets for the variation of the functional δI_l in first order

$$\delta I_l = \int_0^\infty \delta\tilde{\Psi}_l(R) L\Psi_l(R) dR + \int_0^\infty \Psi_l(R) L\delta\tilde{\Psi}_l(R) dR \tag{10}$$

partial integration for the second integral in (10):

$$\int_0^\infty \Psi_l(R) L \delta\tilde{\Psi}_l(R) dR = \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR + \left[\Psi_l(R) \frac{d}{dR} \delta\tilde{\Psi}_l(R) - \delta\tilde{\Psi}_l(R) \frac{d}{dR} \Psi_l(R) \right. \tag{11}$$

variation of the functional:

$$\delta I_l = 2 \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR + \left[\Psi_l(R) \frac{d}{dR} \delta\tilde{\Psi}_l(R) - \delta\tilde{\Psi}_l(R) \frac{d}{dR} \Psi_l(R) \right]_0^\infty \tag{12}$$

use of the boundary conditions (3, 4, 8) and (9) for $\Psi_l(R)$ and $\delta\tilde{\Psi}_l(R)$ in the second part of (12):

$$\delta I_l = 2 \int_0^\infty \delta\tilde{\Psi}_l(R) L \Psi_l(R) dR + k\tilde{\eta}_l \tag{13}$$

under the condition that $\Psi_l(R)$ fulfils (1):

$$\delta I_l = k\tilde{\eta}_l. \tag{14}$$

one defines a new functional:

$$J = I_l + k\eta_l \tag{15}$$

with the exact wavefunction the functional is stationary $(I_l = 0)$

the exact phase shift is calculated from the stationary values of the functional in (15)

in general the exact wavefunction is not known, one uses $\Psi_t(R)$, which depends upon (n+1) parameters and fulfils the conditions in (8 and 9)

plugging the wavefunction into (15), perform differentiation, integration one gets the functional J depending upon (n+1) parameters c_i, η_l:

$$\frac{\partial J}{\partial c_i} = 0 \quad i = 1, 2, ..., n \quad \frac{\partial J}{\partial \eta_l} = k \tag{16}$$

approximate values for the phase shift are calculated by putting $\tilde{\Psi}_t(R)$, with parameters from (16), into (15)

for the asymptotic boundary conditions for the trial wavefunction one can use also other relations:

$$\tilde{\Psi}_l(R) \sim \cos(kR - \frac{l\pi}{2}) + \cot\, \tilde{\eta}_l \sin(kR - \frac{l\pi}{2}) \tag{17}$$

$$\tilde{\Psi}_l(R) \sim \sin(kR - \frac{l\pi}{2}) + \tan\, \tilde{\eta}_l \sin(kR - \frac{l\pi}{2}) \tag{18}$$

finally, one gets for the functional in (9):

$$J = I_l + k \cot \eta_l \tag{19}$$

$$J = I_l + k \tan \eta_l \tag{20}$$

- (20) is the original formulation of Kohn
- the formulation in (19) (Hulthén) is called also the inverse Kohn-method

S-matrix version of the Hulthén-Kohn- variational principle

formulation in 1D: trial functions with incoming and outgoing wave boundary conditions

$$\tilde{\Psi}(R) = -u_0(R) + u_1(R)\tilde{S} + \sum_{i=2}^{N} u_i(R)c_i \tag{21}$$

incoming wave:

$$u_0(R) = v^{-1/2}e^{-ikR} \tag{22}$$

$v = \frac{\hbar k}{\mu}$:asymptotic velocity, wave vector $k = \hbar\sqrt{(2\mu E)}$, $v^{-1/2}$ defines an unit flux for the incoming wave

regularisation of the wavefunction with

$$u_0(R) = f(R)v^{-1/2}e^{-ikR} \tag{23}$$

f(0) = 0 and f(R) = 1 for R$\rightarrow \infty$, the second term in (21) is a product of the

outgoing wave

$$u_1(R) = f(R) v^{-1/2} e^{+ikR} \tag{24}$$

and the approximate S-matrix $\tilde{S}$

third term in (21) defines a set of N square-integrable L^2- basis functions within the interaction region with variational parameters c_i

variation of the trial wavefunction:

$$\tilde{\Psi}(R) = \Psi(R) + \delta\tilde{\Psi}(R) \tag{25}$$

$$\delta\tilde{\Psi}(R) = u_1(R)\delta\tilde{S} + \sum_i \phi_i \delta c_i \tag{26}$$

and plugging into the functional in (5):

$$\int_0^\infty \Psi(R) L \delta\tilde{\Psi}(R) dR = \int_0^\infty \delta\tilde{\Psi}(R) L \Psi(R) dR - \underbrace{\frac{\hbar^2}{2\mu}\left[\Psi(R)\frac{d}{dR}\delta\tilde{\Psi}(R) - \delta\tilde{\Psi}(R)\frac{d}{dR}\Psi(R)\right]_0^\infty}_{Int}$$

with $\delta\tilde{\Psi}(R)$ (26) and $\Psi(R)$ (21) into the second part of the integral:

$$Int = \left(-\frac{\hbar^2}{2\mu}\right)\Big[-\delta\tilde{S}u_0(R)\frac{d}{dR}u_1(R) + u_1(R)\frac{d}{dR}u_1(R)\delta\tilde{S}\tilde{S} + \frac{d}{dR}u_0(R)u_1(R)\delta\tilde{S} - u_1(R)\frac{d}{dR}$$

the part within the parenthesis of the last equation in (27) is $(-2ik/v)$

for the variation of the functional:

$$\delta I_l = 2 \int_0^\infty \delta\tilde{\Psi}(R) L \Psi(R) dR - \frac{\hbar}{i} \delta\tilde{S} \tag{27}$$

define a new functional J:

$$J = \tilde{S} + \frac{i}{\hbar} \int_0^\infty \tilde{\Psi}(R) L \tilde{\Psi}(R) dR \tag{28}$$

in Dirac notation (the 'bra' is not taken complex conjugate)

$$J = \tilde{S} + \frac{i}{\hbar} < \tilde{\Psi}_l(R) | \hat{H} - E | \tilde{\Psi}_l(R) > \tag{29}$$

$$\delta J = \frac{2i}{\hbar} < \delta\tilde{\Psi}(R) | \hat{H} - E | \tilde{\Psi}(R) > \tag{30}$$

variational conditions are now

$$\delta J = 0 \tag{31}$$

if the trial function $\tilde{\Psi}(R)$ is the exact wavefunction and therefore the solution of $(H - E)|\Psi(\mathrm{R}) >= 0$, the S-matrix is $S = \tilde{S} = J$

- we get the S-matrix version of the HKVP as

$$S = \mathrm{ext}\left[\tilde{S} + \frac{i}{\hbar} < \tilde{\Psi}(R)|\hat{H} - E|\tilde{\Psi}(R) >\right] \tag{32}$$

with (21) into (32):

$$S = \frac{i}{\hbar}\mathrm{ext}[< u_0|\hat{H}-E|u_0 > + \sum_{i,i'=1}^{N} c_i c_{i'} < u_i|\hat{H}-E|u_{i'} > -2\sum_{i=1}^{N} c_i < u_i|\hat{H}-E|u_0 >]$$

$$< u_0|\hat{H}-E|u_i >=< u_i|\hat{H}-E|u_0 > \;\; < u_i|\hat{H}-E|u_{i'} >=< u_{i'}|\hat{H}-E|u_i > \quad (33)$$

for $i, i' = 2, N$ and

$$< u_0|\hat{H}-E|u_1 >=< u_1|\hat{H}-E|u_0 > -i\hbar \quad (34)$$

for $i, i' = 1$

for the calculation of the coefficients c_i we perform the variation of (33) as

$$\frac{\partial S}{\partial c_i} = 0, \quad i = 1, ...N \quad (35)$$

- from this we get a set of N linear equations, which can be solved by matrix

inversion, the result is put back into (33) and for the S-matrix follows

$$S = \frac{i}{\hbar}[< u_0|\hat{H}-E|u_0 > - \sum_{i,i'=1}^{N} < u_i|\hat{H}-E|u_0 > (< u_i|\hat{H}-E|u_{i'} >)^{-1} < u_{i'}|\hat{H}-E|u_0 >$$

or in matrix notation:

$$S = \frac{i}{\hbar}(\mathbf{M}_{00} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0) \tag{36}$$

$$M_{00} =< u_0|\hat{H} - E|u_0 > \tag{37}$$

$$(M_0)_i =< u_i|\hat{H} - E|u_0 >, \quad i = 1, ..., N \tag{38}$$

$$(M)_{i,i'} =< u_i|\hat{H} - E|u_{i'} > \quad i = 1, ..., N \tag{39}$$

• in order to simplify the time-consuming inversion of the complex matrix, it is better to separate out the real and imaginary part in (36); this has been done with Feshbach partitioning:

$$S = \frac{i}{\hbar}(\mathbf{B} - \mathbf{C}^T(\mathbf{B}^*)^{-1}\mathbf{C}) \tag{40}$$

$$B = \mathbf{M}_{00} - \mathbf{M}_0^T\mathbf{M}^{-1}\mathbf{M}_0 \tag{41}$$

$$C = \mathbf{M}_{10} - (\mathbf{M}_0^*)^T\mathbf{M}^{-1}\mathbf{M}_0 \tag{42}$$

$$M_{1,0} =< u_0^*|\hat{H} - E|u_0 > \tag{43}$$

• in this S-matrix formulation there are no so-called Kohn-anomalies (found in the K-matrix version of the HKVP)

if the condition

$$\det|\mathbf{M}| = 0 \tag{44}$$

is fulfilled, then in (40) singularities may occur, which result from Siegert eigenvalues (physically correct singularities of the S-matrix for complex energies, they characterise energies and lifetimes of resonances ($E - i\Gamma/2$))

– in the scattering calculations the collision energies are real, and resonances will not occur in the S-matrix

$$K = -2\left(\mathbf{M}_{00} - \mathbf{M}_0^T \mathbf{M}^{-1} \mathbf{M}_0\right) \tag{45}$$

$$S = (1 + iK)(1 - iK)^{-1} \tag{46}$$

– whether one gets problems with singularities depends on the boundary

conditions of u_0 and u_1 for the K-matrix:

$$u_0(R) \sim v^{-1/2} sin(kR) \quad u_1(R) \sim v^{-1/2} cos(kR) \tag{47}$$

– now u_1 is a real function and $\mathbf{M}$ is a real matrix, with real eigenvalues; for some real values of the collision energy E we get singularities in (45)

elastic scattering: the S-matrix is just a number

$$S = \exp(2i\eta) \tag{48}$$

Multi-channel formulation: general aspects

$$S_{n_2,n_1} = ext[c_{1n_2n_1} + \frac{i}{\hbar}\langle\tilde{\Psi}_{n_2}|\hat{H} - E|\tilde{\Psi}_{n_1}\rangle] \tag{49}$$

$\tilde{\Psi}_{n_i}(R)$: trial wave function (regular at $R = 0$) with the asymptotic form (for $R \to \infty$)

$$\tilde{\Psi}^E_{n_i}(R, \{q\}) = \sum_n (-u_{0n_i}(R)\delta_{nn_i} + \sum_{l=1}^{N} u_{ln}(R)c_{ln,n_i})\phi_n(\{q\}). \tag{50}$$

R: translational coordinate, $\{q\}$: coordinates of all internal degrees of freedom with the channel eigenfunctions $\{\phi_n(\{q\})\}$

- this is the multichannel formulation for $\tilde{\Psi}(R, \{q\})$ which can be used for elastic (without $\{q\}$ and ϕ_{n_i}), inelastic and reactive processes (with introduction of the

indices 1,2 for the arrangements A + BC and AB + C in the collinear case)
– $\{u_{ln}(R)\}, l = 2, .., N$ is a square integrable basis set
– $u_{0n}(R)$ and $u_{1n}(R)$ have the properties of incoming and outgoing waves, which can be "free" functions (the special form depends on the dimension of space to be included) or distorted functions
– in order to regularize u_{0n} and u_{1n} ($u_{1n} = u_{0n}^*$), they are multiplied by a cutoff function f(R)
– in case of collinear reaction one chooses

$$u_{0n} = f(R)e^{-ik_nR}v_n^{-\frac{1}{2}}, \quad v_n = \frac{\hbar k_n}{\mu}, \quad k_n = (\frac{2\mu(E-E_n)}{\hbar^2})^{\frac{1}{2}} f(R) = \frac{1}{2}\{1 + tanh[\alpha(R -$$

– stationarity of (49) with respect to the expansion coefficients c_{ln_i,n_j} (in (50))

leads to the matrix equation

$$\mathbf{S} = \frac{\mathbf{i}}{\hbar}(\mathbf{B} - \mathbf{C^T}\mathbf{B}^{*-1}\mathbf{C}) \tag{52}$$

$\mathbf{S}, \mathbf{B}$ and $\mathbf{C}$: matrices of the size of the number of open channels

$$\mathbf{B} = \mathbf{M_{00}} - \mathbf{M_0^T}\mathbf{M^{-1}}\mathbf{M_0} \tag{53}$$

$$\mathbf{C} = \mathbf{M_{10}} - \mathbf{M_0^{*T}}\mathbf{M^{-1}}\mathbf{M_0} \tag{54}$$

$$(M_{00})_{nn'} = \langle u_{0n}\phi_n|\hat{H} - E|u_{0n'}\phi_{n'}\rangle \tag{55}$$

$$(M_{10})_{nn'} = \langle u_{1n}\phi_n|\hat{H} - E|u_{0n'}\phi_{n'}\rangle \tag{56}$$

$$(M)_{ln,l'n'} = \langle u_l\phi_n|\hat{H} - E|u_{l'}\phi_{n'}\rangle, \quad l,l' = 2,..,N \tag{57}$$

$$(M_0)_{ln,n'} = \langle u_l\phi_n|\hat{H} - E|u_{0n'}\phi_{n'}\rangle, \quad l = 2,..,N \tag{58}$$

– the translational functions in the bra symbols in (55,56) are not the complex conjugate ones, n: collective index of all internal quantum numbers

• the main numerical effort in this scattering method is the calculation of matrix elements

– those in (55,56,58) have to be recalculated for each energy

– the matrix elements of the Hamiltonian and the overlap matrix over the basis $u_l\phi_n,\ l \geq 2$, in (57) have to be calculated only once, but the inversion of $\mathbf{M}$ has to be repeated for each energy

• in our work the wavefunction ($u_{ln}\phi_n,\ l \geq 2$) is built up from FE-functions in the interior region and analytical functions ($u_{ln},\ l \leq 1$) in the asymptotic region

– we first solve the eigenvalue problem within FEM in 2D, resp. 3D

$$(\Psi^{FEM}|\hat{H}|\Psi^{FEM}) = E'(\Psi^{FEM}|\Psi^{FEM}) \tag{59}$$

up to a maximum eigenvalue E_{max} or up to a finite number of eigenfunctions, which are then used as a new orthogonal basis for calculating the matrix elements in (57) and (58)

– the inversion of the large matrix $\mathbf{M}$ for different collision energies is then just the inversion of the diagonal elements

• in order to reduce the size of the matrices in (53 - 58), different polynomial orders for finite elements and different potential adapted basis sets have been tested

S-matrix version of the HKVP: 3D formalism

atom-diatom system with three arrangements α: (A + BC, B+ AC, C + AB)
(R_α,q_α, arrangement α)

$\phi_{\alpha\mathbf{n}}$:asymptotic internal eigenfunctions of $\hat{H}_\alpha$ with asymptotic potential energy v_α for this arrangement:

$$\hat{H}_\alpha = \hat{H} - [-\frac{\hbar^2}{2\mu_\alpha}\frac{1}{R_\alpha}\frac{\partial^2}{\partial R_\alpha^2}R_\alpha] - V + v_\alpha,\ v_\alpha = \lim_{R_\alpha\to\infty} V \qquad (60)$$

$\alpha\mathbf{n}$: complete set of quantum numbers which characterize the channel. $u_{0\alpha\mathbf{n}}(R_\alpha)$: asymptotically incoming translational function for channel $\alpha\mathbf{n}$

$$\lim_{R_\alpha\to\infty} R_\alpha u_{0\alpha\mathbf{n}}(R_\alpha) \sim v_{\alpha\mathbf{n}}^{-1/2} e^{-i(k_{\alpha\mathbf{n}}R_\alpha - (\pi/2)l_{\alpha\mathbf{n}})}\ k_{\alpha\mathbf{n}} \equiv \mu_\alpha v_{\alpha\mathbf{n}} = \sqrt{2\mu_\alpha(E-\epsilon_{\alpha\mathbf{n}})}/\hbar$$

$k_{\alpha\mathbf{n}}$ and $l_{\alpha\mathbf{n}}$: wave vector and orbital angular momentum for the channel $\alpha\mathbf{n}$;

$u_{0\alpha\mathbf{n}}(R_\alpha)$ and $u_{1\alpha\mathbf{n}}(R_\alpha)$ as before

expansion of the scattering wave:

$$\Psi_{\alpha_1\mathbf{n_1}} = \sum_{\alpha\mathbf{n}} \phi_{\alpha\mathbf{n}}(q_\alpha)[-u_{0\alpha\mathbf{n}}(R_\alpha)\delta_{\alpha\alpha_1}\delta_{\mathbf{n}\mathbf{n_1}} + \sum_{t=1}^{N} u_{t\alpha\mathbf{n}}(R_\alpha)c_{t\alpha\mathbf{n},\alpha_1\mathbf{n_1}}] \qquad (61)$$

$\alpha_1\mathbf{n_1}$: initial channel, $c_{t\alpha\mathbf{n},\alpha_1,\mathbf{n_1}}$: variational parameters

asymptotic form of the wavefunction

$$\lim_{R_\alpha\to\infty} R_\alpha\Psi_{\alpha_1\mathbf{n_1}} \sim \sum_{\alpha\mathbf{n}} \phi_{\alpha\mathbf{n}}(q_\alpha)v_{\alpha\mathbf{n}}^{-1/2}\times[-e^{-i(k_{\alpha\mathbf{n}}R_\alpha-(\pi/2)l_{\alpha\mathbf{n}})}\delta_{\alpha\alpha_1}\delta_{\mathbf{n}\mathbf{n_1}}+e^{i(k_{\alpha\mathbf{n}}R_\alpha-(\pi/2)l_{\alpha\mathbf{n}})}S_{\alpha\mathbf{n},\alpha_1\mathbf{n_1}}] \qquad (62)$$

q_α: for a given arrangement $q_\alpha = (r_\alpha, \hat{R}_\alpha)$ with r_α as the relative diatomic coordinate vector

n: (vjlJM), (v,j): vibrational and rotational quantum numbers of the atom relative to the diatom, l: orbital angular momentum of the atom relative to the diatom, (J,M): total angular momentum and its projection onto a space fixed axis, the matrices are diagonal in J and M

channel eigenfunctions $\phi_{\alpha\mathbf{n}}$:

$$\phi_{\alpha\mathbf{n}}(q_\alpha) = \phi^{JM}_{\alpha vjl}(r_\alpha, \hat{R}_\alpha) = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} (-1)^{j+M} f_{vj}(r_\alpha) \sum_k C(jJl; k, -k)\Psi_{jk}(\gamma_\alpha) D^J_{Mk}(A, B,$$

(63)

$f_{vj}(r_\alpha)$: diatomic vibrational eigenfunction, C: Clebsch-Gordan coefficients, $\Psi_{jk}(\gamma_\alpha)$: associated Legendre polynomial, γ_α: angle between r_α and $\hat{R}_\alpha$, D^J_{Mk}: Wigner rotation matrix

– the matrix elements of $(\hat{H} - E)$ between typical basis functions $u_{t\alpha}(R_\alpha)\phi^{JM}_{\alpha vjl}(r_\alpha, \hat{R}_\alpha)$ are evaluated as usually

– Euler angles (A, B, Γ). are integrated out analytically, rest is done numerically

- general expression for the matrix elements is

$$(M)^{J}_{t'\alpha'v'j'l',t\alpha vjl} =< u_{t'\alpha'}\phi^{JM}_{\alpha'v'j'l'}|\hat{H} - E|u_{t\alpha}\phi^{JM}_{\alpha vjl} >=$$

$$(-1)^{j'+j}\sum_{k,k'} C(j'Jl';k',-k')C(jJl;k',-k)$$

$$\times \int d\tau u_{t'\alpha'}(R_{\alpha'})f_{\alpha'v'j'}(r_{\alpha'})\Psi_{j'k'}(\gamma_{\alpha'})d^{J}_{k'k}(\gamma_{\alpha'\alpha})R^{-1}_{\alpha}$$

$$\times[-\frac{\hbar^2}{2\mu_\alpha}\frac{d^2}{dR^2_\alpha} + \frac{\hbar^2 l(l+1)}{2\mu_\alpha R^2_\alpha} + \epsilon_{\alpha vj} + V - v_\alpha - E]R^{-1}_{\alpha}u_{t\alpha}(R_\alpha)f_{\alpha vj}(r_\alpha)\Psi_{jk}(\gamma_\alpha) \quad (64)$$

$d\tau$: three-dimensional volume element ($d\tau = r^2_\alpha R^2_\alpha \sin\gamma_\alpha \; dr_\alpha dR_\alpha d\gamma_\alpha$)

$\gamma_{\alpha',\alpha}$: angle between the two vectors $\hat{R}_{\alpha'}$ and $\hat{R}_\alpha$

$\epsilon_{\alpha vj}$: rovibrational eigenvalues of potential v_α

μ_α: translational reduced mass for channel α

– integration variables can be chosen in a variety of ways

because we do the scattering calculations (reactive and non reactive) only with one Jacobi coordinate, the angle $\gamma_{\alpha'\alpha}$ is identically zero:

$$d^J_{k'k}(\gamma_{\alpha'\alpha}) \rightarrow d^J_{k'k}(0) = \delta_{k,k'}, \tag{65}$$

(64) reduces to a single sum

no exchange matrix elements, those with $\alpha' \neq \alpha$

(64) applies for t and $t' = 0$ or 1: "free" translational function, for $\mathbf{M}_{00}$, $\mathbf{M}_{10}$, $\mathbf{M}_0$

for L^2 functions: $t, t' > 2$ for the matrix **M**.

$u_{0\alpha vjl}(R_\alpha)$: spherical Hankel functions

– regular and irregular parts multiplied with different cut-off functions (f_1, f_2)

$$R_\alpha u_{0\alpha vjl}(R_\alpha) = v_{\alpha vj}^{-1/2}(k_{\alpha vj}R_\alpha) \times [f_1(R_\alpha)n_l(k_{\alpha vj}R_\alpha) - if_2(R_\alpha)j_l(k_{\alpha vj}R_\alpha)]$$

j_l and n_l: regular and irregular spherical Bessel functions

3D potential adapted basis functions from 3D eigenvalue calculations

– solution of the 3D eigenvalue problem (interior region of the ABC -system)

– general formalism introduced by Sutcliffe et al.

• body-fixed Hamiltonian:

$$\hat{H} = K_V + K_{VR} + V(r, R, \gamma) \tag{66}$$

V: electronic potential, K_V and K_{VR} include different vibrational (V) and rotational (R) terms

• symmetrized angular basis functions:

$$|j,k> = 2^{-1/2}(1+\delta_{k0})^{-1/2}[\Psi_{jk}(\gamma)D^J_{Mk}(A,B,\Gamma)+(-1)^p\Psi_{j-k}(\gamma)D^J_{M-k}(A,B,\Gamma)] \tag{67}$$

the total parity is given by $(-1)^{J+p}$ with $p = 0$ or 1 for e or f states, respectively

- effective kinetic energy operator ($J = 0$):

$$K_V = \delta_{j'j}\delta_{k'k}\left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2}j(j+1)\left(\frac{1}{\mu_1 r^2} + \frac{1}{\mu_2 R^2}\right)\right] \qquad (68)$$

μ_1 and μ_2 are the usual reduced masses in Jacobi coordinates

- Ansatz for the wavefunction of E_l^J:

$$\Psi_l^J = \sum_k \sum_{jmn} d_{kjmn}^{Jl} |j,k> |m> |n> \qquad (69)$$

– radial basis functions for r and R ($|m> |n>$)

– symmetrized angular basis functions $(|j,k>)$

• FEM: instead of $|m> |n>$ a new set $|mn>$ (no separation in r and R)

homonuclear diatomics: wavefunction is symmetric or antisymmetric with respect to interchange of the like atoms, j even and odd are symmetric and antisymmetric

• we start with the 2D solution in r and R: for a given angle γ

$$\hat{H}(r,R) = K_V + K_{VR} + \delta_{k'k} < j',k|V(r,R,\gamma)|j,k >_\gamma \tag{70}$$

– appropriate angular functions

$$|j,k >= \Psi_{j,k}(\gamma)|J,M,k > \tag{71}$$

$|J,M,k>$: total angular momentum eigenfunctions

• transformation of the Hamiltonian of (70) to a discrete variable representation (DVR) in γ:

$$\underline{\underline{H}}^{DVR} = \underline{\underline{T}}^{T}\,\underline{\underline{H}}\,\underline{\underline{T}} \tag{72}$$

$$T^{k}_{j\alpha} = \omega^{1/2}_{k\alpha}\Psi_{jk}(\gamma_{k\alpha}) \tag{73}$$

$\underline{\gamma}_k$ and $\underline{\omega}_k$: points and weights of an N-point Gauss-associated Legendre quadrature points of order k

• contribution due to the potential, which is diagonal in the DVR:

$$\sum_{j,j'=k}^{N+k-1} T^{k}_{j'\alpha'} < j'k|V(r,R,\gamma)|j,k >_{\gamma} T^{k}_{j\alpha} \simeq \delta_{\alpha\alpha'}V(r,R,\gamma_{k\alpha}) \tag{74}$$

- angular off-diagonal contributions:

$$L^k_{\alpha\alpha'} = \sum_{j=k}^{N+k-1} T^k_{j'\alpha'} j(j+1) T^k_{j'\alpha} \tag{75}$$

- resulting $J = k = 0$ effective radial Hamiltonian:

$$\hat{H}_{\alpha\alpha'} = \delta_{\alpha\alpha'} \left[-\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial R^2} + V(r, R, \gamma_{k\alpha}) \right] + \frac{\hbar^2}{2}\left(\frac{1}{\mu_1 r^2} + \frac{1}{\mu_2 R^2} \right) L^0_{\alpha\alpha'} \tag{76}$$

Strategy:
(1) solve the effective radial Hamiltonian for each α on the DVR grid by using finite elements

(2) lowest solutions, selected either by number or energy cut off, are then used to construct a full 3D Hamiltonian matrix which is diagonalised to yield the eigenenergies and values for the wavefunctions at the DVR grid points

– with permutation symmetry of like atoms as in AB_2 systems:

$$L^{kq}_{\alpha\alpha'} = 2 \sum_{j=k}^{N/2+k-1} T^k_{2j+q,\alpha'}(2j+q)(2j+q+1)T^k_{2j+q,\alpha}\ q = 0, 1 \qquad (77)$$

Distorted waves

- reduction of computer time:

– reduce the number of basis functions in the interaction region

– reduce the number of functions in the asymptotic region

- idea: solve first the inelastic problem with a close-coupling method (Groenenboom et al) and coupling with FE

CC-method: wavefunction $\chi_j(R, r, \theta)$ is expanded in basis functions $\phi_i(r, \theta)$ for each scattering channel, which describe rotation (j_i) and vibration (v_i) along the reaction coordinate R

system of coupled equations for the translational matrix function $U_{ij}(R)$

solution by a propagation method (renormalized Numerov method)

separation of the different arrangement channels: distortion potential in the area R $<$ Rmax

two different distortion potentials: two different solutions

linear combination of the distorted inelastic waves: to get incoming and outgoing waves for the HKVP

inelastic waves fulfil SE in the area $R = \infty \rightarrow R_{\text{max}}$

close-coupling solutions overlap with the L^2-basis functions

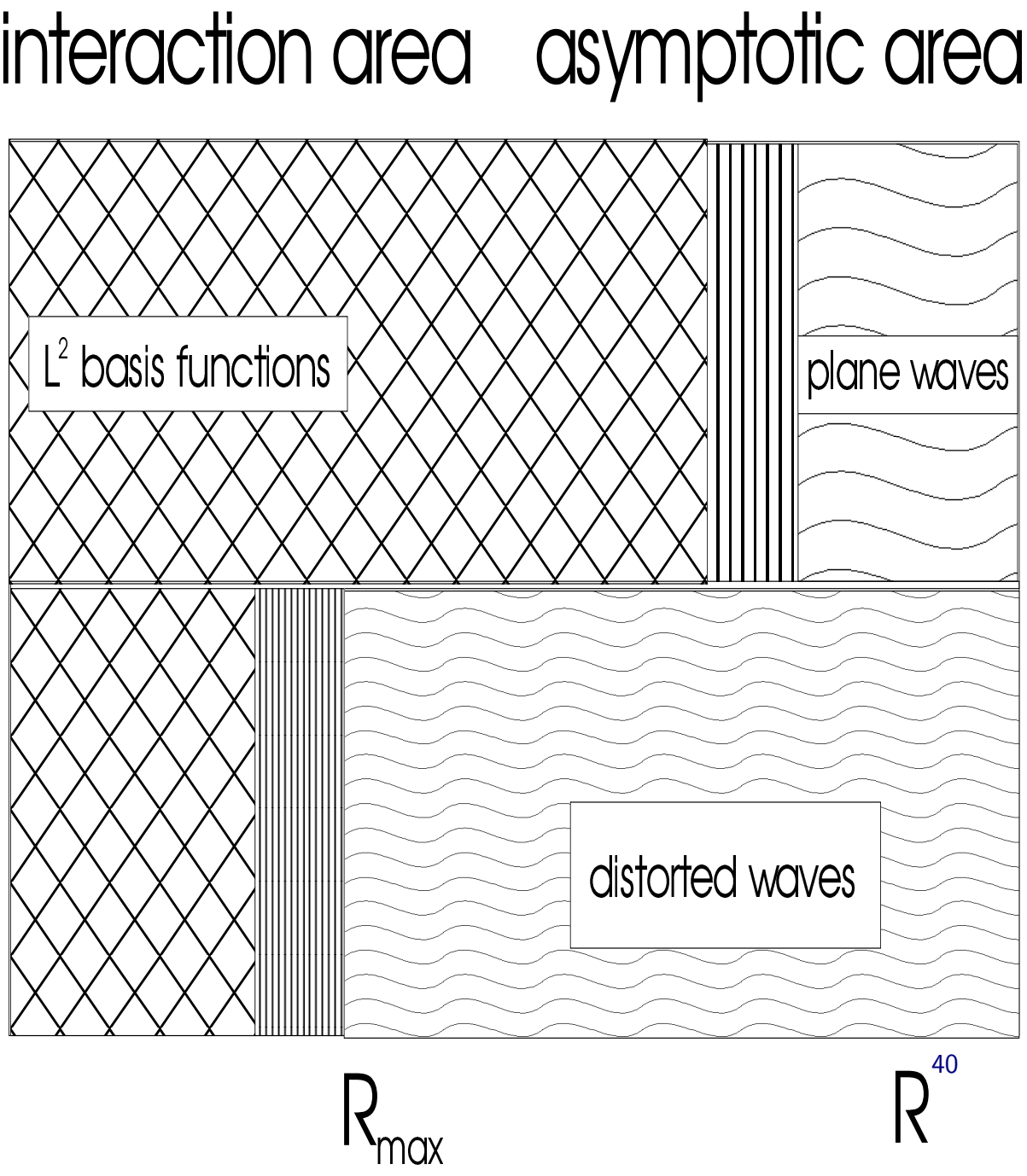


Figure 1: Separation of the potential area into parts for the L^2 basis functions and the plane or distorted waves

Advantages:

- We do not need cut-off functions any more. The distorted wave automatically describe the boundary conditions at $R = 0$.
- Reduction of the area for the L^2 basis functions.
- $(H - E)$ operating on the distorted waves (see (108)) is only a multiplicative operation and easy to calculate.

Numerov method for distorted waves

close-coupling equation for $U_{ij}(R)$ along the translational direction R (Jacobi coordinate), inelastic atom-diatom collision ($J = 0$) in three dimensions:

$$(\hat{H} - E)\frac{\chi_j(R, r, \theta)}{Rr} = 0 \tag{78}$$

χ_j: expansion $\phi_i(r, \theta)$

$$\chi_j(R, r, \theta) = \sum_{i=1}^{n_{tot}} \phi_i(r, \theta) U_{ij}(R); j = 1, 2, .., \mathsf{n}_{tot} \tag{79}$$

n_{tot}: sum of open and closed channels

i: collective index for the rotational j_i and vibrational quantum number v_i

(78 and 79): multiplication from the left with the asymptotic eigenfunctions $\phi_i(r,\theta)$, integration over r and θ:

$$\frac{\partial^2}{\partial R^2}\mathbf{U}(R) = \mathbf{W}(R)\mathbf{U}(R) \tag{80}$$

$$W_{ij} = \frac{2\mu}{\hbar^2} < \phi_i|V(R,r,\theta) - V(\infty,r,\theta)|\phi_j > + [\frac{j_i(j_i+1)}{R^2} - k_i^2]\delta_{ij} \tag{81}$$

solution at the grid point R_k:

$$R_k = R_0 + k\Delta;\ k = 1, ..., \text{nstep} \tag{82}$$

U_k (i,j left out for simplification) is defined as $U(R_k)$

Numerov propagator (Milnes correction formula):

$$U_k = 2U_{k-1} - U_{k-2} + \frac{\Delta^2}{12}(W_k U_k + 10 W_{k-1} U_{k-1} + W_{k-2} U_{k-2}) \tag{83}$$

equivalent to

$$(I - \frac{\Delta^2}{12} W_k) U_k - 2(I + \frac{5\Delta^2}{12} W_{k-1}) U_{k-1} + (I - \frac{\Delta^2}{12} W_{k-2}) U_{k-2} = 0 \tag{84}$$

- direct propagation of the U-matrix can be numerically difficult
- to get converged results for $\mathbf{U}$: closed channels have to be included
- leads to large values within the U_k matrix

• easier to propagate: Q_k

$$Q_k = U_{k-1} U_k^{-1} \tag{85}$$

$$F_k = I - \frac{\Delta^2}{12} W_k \tag{86}$$

$$Q_k = [12I - 10F_{k-1} - F_{k-2}Q_{k-1}]^{-1} F_k \tag{87}$$

- from $U_0 = 0$ and $U_1 \neq 0$: $Q_1 = 0$
- recursion formula (87): $Q_2, Q_3, ..., Q_{\text{nstep}}$
- with (85): U-matrix can be calculated back from U_{nstep} to U_1

U_{nstep} will be calculated from the asymptotic behaviour of U_1:

$$U_{ij}(R) \sim v_i^{-1/2} [\cos(k_i R - \frac{\pi j_i}{2}) K_{ij} + \sin(k_i R - \frac{\pi j_i}{2})) \delta_{ii}] \quad \text{open channels} \tag{88}$$

$$U_{ij}(R) \sim |v_i|^{-1/2}[\exp(-|k_i|R)K_{ij} + \exp(|k_i|R))\delta_{ii}] \quad \text{closed channels} \tag{89}$$

$\{K_{ij}\}$ is the K-matrix

- Reformulation:

$$U_{ij}(R) = C_{ij}(R)K_{ij} + C_{ij}(R) \tag{90}$$

$$C_{ii}(R) = |v_i|^{-1/2}(\cos(k_iR - \frac{\pi j_i}{2})) \tag{91}$$

$$S_{ii}(R) = |v_i|^{-1/2}(\sin(k_iR - \frac{\pi j_i}{2}))\delta_{ii} \tag{92}$$

At $R = R_k$:

$$U_k = C_kK + S_k \tag{93}$$

for the K- and S-matrix:

$$K = -[Q_k C_k - C_{k-1}]^{-1}[Q_k S_k - S_{k-1}] \tag{94}$$

$$S = (I + iK)(I - iK)^{-1} \tag{95}$$

- modification of the starting problem: $V_\alpha^{(p)}(R_\alpha)$ $(p = 1, 2)$, two independent solutions $\chi_n^{(p)}$

$$[\hat{H} - E + V_\alpha^{(p)}(R_\alpha)]\chi_n^{(p)}(q_\alpha) = 0 \; p = 1, 2; \; q_\alpha = (R_\alpha, r_\alpha, \theta_\alpha) \tag{96}$$

$$\chi_n^{(p)}(q_\alpha) = \sum_{n'} \phi_{n'}(r_\alpha, \theta_\alpha) U^p_{n',n}(R_\alpha) \tag{97}$$

n: all open, n' all open and closed channels

– asymptotically(see (88)):

$$U^{(p)}(R_\alpha) \sim C(R_\alpha) + S(R_\alpha)K^{(p)} \tag{98}$$

incoming and outgoing waves (H^-, H^+) with S-matrix boundary conditions:

$$\begin{aligned} H^{(+)} &= C(R_\alpha) + S(R_\alpha)K^{(p)} \\ H^{(-)} &= C(R_\alpha) - S(R_\alpha)K^{(p)} \end{aligned} \tag{99}$$

then

$$U^{(p)}A^{(p)} \sim -H^{(-)}S^{(p)\dagger} + H^{(+)} \tag{100}$$

$$A^{(p)} = 2(-I + iK^{(p)})^{-1}$$

$$S^{(p)\dagger} = (-I - iK^{(p)})(-I + iK^{(p)})^{-1}$$

Subtraction of (100) with $p = 2$ from the one with $p = 1$:

$$U^{(1)}A^{(1)} - U^{(2)}A^{(2)} \sim H^{(-)}(S^{(2)\dagger} - S^{(1)\dagger}) \tag{101}$$

with

$$\Delta = S^{(2)\dagger} - S^{(1)\dagger} \tag{102}$$

$$E^{(1)} = A^{(1)}(\Delta^{\dagger})^{-1} \tag{103}$$

$$E^{(2)} = -A^{(2)}(\Delta^{\dagger})^{-1} \tag{104}$$

one gets

$$U^{(1)}E^{(1)} + U^{(2)}E^{(2)} \sim H^{(-)} \tag{105}$$

– inelastic waves with boundary solutions for incoming and outgoing waves:

$$\chi_n(q_\alpha) = \sum_{p=1}^{2} \sum_{n'} \chi_{n'}^{(p)}(q_\alpha) E_{n',n}^{(p)} \tag{106}$$

n, n:: only open channels

$(\mathbf{M}_0)_{in,n'}$-matrix elements:

from (96):

$$(\hat{H} - E)\chi_n = -V_{(\alpha)}^{(p)} \chi_n^{(p)} \tag{107}$$

with (106):

$$(\hat{H} - E)\chi_n = -\sum_{p=1}^{2} V_{(\alpha)}^{(p)}(R) \sum_{n'} \chi_{n'}^{(p)} E_{n',n}^{(p)} \tag{108}$$

– FEM and Numerov grid points not identical: interpolation

$(\mathrm{M}_0)_{in,n'}$: at the FEM grid points, interpolate the values for $\mathrm{U}(\mathrm{R}_i)$

$U_i^{(p)} = U^{(p)}(R_i), R_i = ih, i = n_0, n_0 + 1..., n_1$

$R_a = R_{i-1} + ah$ with $b = 1 - a$; R_{i-1} and R_i are original grid points

$$U(R_a) = bU_{i-1} + aU_i + \frac{ab(a-2)h^2}{6} W_{i-1}U_{i-1} + \frac{ab(b-2)h^2}{6} W_i U_i. \qquad (109)$$

$(\mathbf{M}_{0,0})_{n,n'}$-matrix elements:

$$\begin{aligned}(M_{0,0})_{n,n'} &= <\chi_n|\hat{H}-E|\chi_{n'}> \\ &= \sum_{p=1}^{2}\sum_{q=1}^{2}\sum_{m}\sum_{m'} E^{(p)}_{m,n}E^{(q)}_{m',n}X^{(p,q)}_{m,m'}\end{aligned} \tag{110}$$

with

$$X^{(p,q)}_{m,m'} = -\int_0^\infty dR V^q_{(\alpha)}(R)\sum_n U^{(p)}_{n,m}(R)U^{(q)}_{n,m'}(R) \tag{111}$$

n: open and closed channels

Distortion potential:

• to prevent the overlap of the incoming inelastic waves of the different arrangements:

– the distortion potential should be repulsive at short distances ($R < R_{\text{max}}$)

– for $R \geq R_{\text{max}}$ the potential is zero

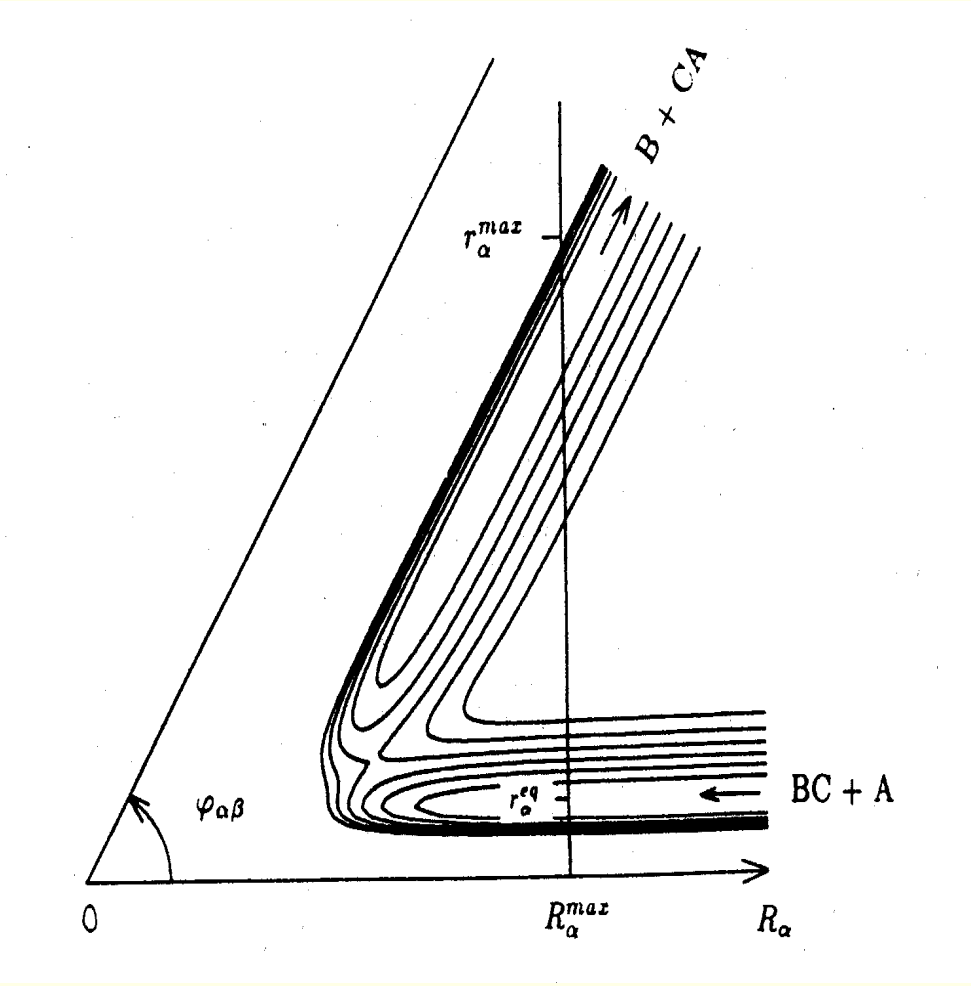
– for R_{max} the potential should be chosen such that the interaction region becomes small so that not too many L^2-basis functions or finite element grid points are needed

– the distortion potential should not increase too much, otherwise the calculation of $(\mathsf{M}_0)_{in,n'}$ needs too many interpolation grid points

$$V_\alpha^{(p)} = \begin{cases} a_p(R - R_{\text{max}})^4, & R < R_{\text{max}}, \\ 0, & R \geq R_{\text{max}} \end{cases} \tag{112}$$

II.3 The hyperspherical method

Figure 2: Potential energy contours for an atom-diatom reaction. The Jacobi coordinates of arrangement α are sketched.



numerical calculation of the wavefunction Ψ^{JM}

$$\Psi^{JM}_{\lambda vjl} = \sum_{\lambda' v' j' l'} \frac{1}{R_{\lambda'}} f^{J}_{\lambda' v' j' l' \lambda vjl}(R_{\lambda'}) \Phi^{JM}_{\lambda' v' j' l'}(\mathbf{r}_{\lambda'} \hat{\mathbf{R}}_{\lambda'}) \tag{113}$$

analysis of its asymptotic behaviour at large atom-diatom distance

$$\begin{aligned} f^{J}_{\lambda' v' j' l' \lambda vjl}(R_{\lambda'}) \rightarrow & \frac{1}{k^{1/2}_{\lambda vj}} e^{-i(k_{\lambda vj} R_{\lambda} - l\pi/2)} \delta_{\lambda' \lambda} \delta_{v' v} \delta_{j' j} \delta_{l' l} \\ & - \frac{1}{k^{1/2}_{\lambda' v' j'}} e^{-i(k_{\lambda' v' j'} R_{\lambda'} - l'\pi/2)} S^{J}_{\lambda' v' j' l' \lambda vjl} \end{aligned} \tag{114}$$

in each arrangement λ permits the evaluation of the K and S matrices

- appearance of different Jacobi coordinate systems in the asymptotic behaviour

renders reactive scattering calculations more complicated than inelastic scattering calculations, for which only one set of Jacobi coordinates is needed

- calculation of the wavefunction in the reaction region needs to be performed with a different type of expansion

- collinear expansion of ψ, Jacobi coordinates in arrangement α:

$$\Psi = \sum_v \chi_{\alpha v}(r_\alpha) f_v(R_\alpha) \tag{115}$$

$\chi_{\alpha v}(r_\alpha)$: solutions of the $asymptotic$ Hamiltonian of arrangement α

$$[-\frac{1}{2\mu}\frac{\partial^2}{\partial r_\alpha^2} + v_\alpha(r_\alpha)]\chi_{\alpha v}(r_\alpha) = \varepsilon_\alpha \chi_{\alpha v}(r_\alpha) \tag{116}$$

$v_\alpha(r_\alpha)$: C diatom potential, the limit of the potential energy function $V(R_\alpha, r_\alpha)$ when $R_\alpha \to \infty$

- f should be integrated from 0 to some limit $R_\alpha^{\max}$ situated in the region where the interaction potential has reached its asymptotic behaviour in both arrangements α and β

- a large number of eigenstates $\chi_{\alpha v}(r_\alpha)$ are needed to represent accurately the wavefunction in arrangement β because vibrational wavefunctions with a small v quantum number are localized near the minimum r_α^{eq} of the potential $v_\alpha(r_\alpha)$

- the number of bound vibrational states for a molecular potential is finite, a continuum of states $\chi_{\alpha\epsilon}(r_\alpha)$ with positive energy should also be included in the close-coupling expansion

- one may use an expansion over eigenstates which are adapted to the $true$

potential and not to the $asymptotic$ potential

- one thus defines $adiabatic\ states$ by solving for each R_α:

$$[-\frac{1}{2\mu}\frac{\partial^2}{\partial r_\alpha^2} + V(R_\alpha, r_\alpha)]\chi_{\alpha v}(R_\alpha; r_\alpha) = \varepsilon_\alpha(R_\alpha)\chi_{\alpha v}(R_\alpha; r_\alpha) \qquad (117)$$

- the first eigenstates of (117) concentrate into regions of low potential energy and thus will conveniently 'fill' the two arrangement valleys at large R_α

- the part of the wavefunction which goes into arrangement α is very well represented by an expansion over these eigenstates

- this is however not the case for the part of the wavefunction which goes into arrangement β

- the wavefunction Ψ is roughly localized between two equipotentials corresponding to the total energy E
- lines of constant R_α cut these equipotentials obliquely, the length in the r_α coordinate is larger than in the r_β coordinate
- solving a SE on a larger range of the variable means more effort and also more states to reach the limits of the domain of definition of the wavefunction
- this difficulty is most pronounced for large skew angles $\varphi_{\alpha\beta}$ (i.e. for light-heavy-light collisions)
- for very small skew angles (heavy-light-heavy collisions), this difficulty does not appear and the expansion over the $\chi_{\alpha v}(R_\alpha; r_\alpha)$ states is a viable alternative

- minimizing the number of basis states in each arrangement requires a coordinate system in which lines of constant values of the propagation variable cut the arrangement valleys at right or almost right angles, for large values of the propagation variable

- such coordinate systems are obviously $curvilinear$

- the simplest of the coordinate systems which satisfies these requirements is ($polar$ coordinates)

$$\rho = \sqrt{R_\alpha^2 + r_\alpha^2} \qquad\qquad \omega = \arctan \frac{r_\alpha}{R_\alpha} \tag{118}$$

  in 3D: generalization of polar coordinates yields the hyperspherical coordinates of six-dimensional space

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} -\sqrt{\frac{m_A m_B}{(m_A+m_C)(m_C+m_B)}} & -\sqrt{\frac{m_C(m_A+m_B+m_C)}{(m_A+m_C)(m_C+m_B)}} \\ \sqrt{\frac{m_C(m_A+m_B+m_C)}{(m_A+m_C)(m_C+m_B)}} & -\sqrt{\frac{m_A m_B}{(m_A+m_C)(m_C+m_B)}} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix} \quad (119)$$

or

$$\begin{pmatrix} \mathbf{R}_\beta \\ \mathbf{r}_\beta \end{pmatrix} = \begin{pmatrix} \cos\,\phi_{\alpha\beta} & \sin\,\phi_{\alpha\beta} \\ -\sin\,\phi_{\alpha\beta} & \cos\,\phi_{\alpha\beta} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\alpha \\ \mathbf{r}_\alpha \end{pmatrix} \quad (120)$$

$$\tan\phi_{\alpha\beta} = m_C/\mu,\ \varphi_{\alpha\beta} = \phi_{\alpha\beta} - \pi,\ \phi_{\alpha\beta} = [\pi, 3\pi/2] \quad (121)$$

– Transformation from one (mass-weighted) Jacobi coordinate to the other is a mere rotation, the $hyperradius$ $\rho = \sqrt{R_\alpha^2 + r_\alpha^2}$ does not depend on the arrangement index λ

– a set of five hyperangles denoted collectively as Ω completes the description of configuration space

Hyperradial equations

Six-dimensional Laplacian:

$$\overrightarrow{\nabla}^2_{R_\lambda} + \overrightarrow{\nabla}^2_{R_\lambda} \equiv \frac{1}{\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} - \frac{\Lambda^2(\Omega)}{\rho^2} \tag{122}$$

$\Lambda^2(\Omega)$: the $grand-angular\ momentum$

explicit analytical form depends on the choice of hyperangles

$\Lambda^2(\Omega)$ commutes with $\overrightarrow{J}^2$ and J_z

Hamiltionian:

$$H \equiv -\frac{1}{\mu\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} + \frac{\Lambda^2(\Omega)}{2\mu\rho^2} + V(\rho,\Omega) \tag{123}$$

Eigenfunctions of Λ^2 are called hyperspherical harmonics.

They form a complete set of eigenfunctions in Ω-space and can be used to represent the variation of $\Psi(\rho, \Omega)$ at fixed ρ.

Many of them are in general needed to represent the wavefunction accurately, especially at large ρ.

The adiabatic representation

fixed-ρ Hamiltonian:

$$H(\rho) = \frac{\Lambda^2(\Omega)}{2\mu\rho^2} + V(\rho, \Omega) \tag{124}$$

define a set of $potential\ adapted$ adiabatic states $\Phi_k^{JM}(\rho; \Omega)$, (eigenfunctions of $H(\rho)$:)

$$H(\rho)\Phi_k^{JM}(\rho; \Omega) = \epsilon_k^J(\rho)\Phi_k^{JM}(\rho; \Omega) \tag{125}$$

partial wave Ψ^{JM} can be expanded over the $\Phi_k^{JM}(\rho; \Omega)$ states:

$$\Psi^{JM} = \frac{1}{\rho^{5/2}} \sum_k \Phi_k^{JM}(\rho; \Omega) f_k^J(\rho) \tag{126}$$

hyperradial components $f_k^J(\rho)$ are the solutions of a set of coupled second order

differential equations:

$$[-\frac{1}{2\mu}\frac{d^2}{d\rho^2}+\epsilon_k^J(\rho)+\frac{15}{8\mu\rho^2}-E]f_k^J(\rho)\ -\frac{1}{2\mu}\sum_{k'}[2P_{kk'}^J(\rho)\frac{df_{k'}^J}{d\rho}+Q_{kk'}^J(\rho)\ f_{k'}^J]=0 \tag{127}$$

$non-adiabatic$ couplings in (127) are given by

$$P_{kk'}^J(\rho)=<\Phi_k^{JM}(\rho;\Omega)|\frac{\partial}{\partial\rho}\Phi_{k'}^{JM}(\rho;\Omega)>_\Omega \tag{128}$$

$$Q_{kk'}^J(\rho)=<\Phi_k^{JM}(\rho;\Omega)|\frac{\partial^2}{\partial\rho^2}\Phi_{k'}^{JM}(\rho;\Omega)>_\Omega \tag{129}$$

- large density of states Φ_k^{JM}, numerous avoided crossings occur between adiabatic curves $\epsilon_k^J(\rho)$

- Φ_k^{JM} have to be evaluated on a very fine grid of ρ to yield an accurate representation of the P and Q couplings

- (127) in general difficult to integrate numerically.

The diabatic representation

instead an adiabatic representation: better to use a $diabatic$ representation (expansion over constant states, in small sectors $[\rho_p^{(l)}\rho_p^{(r)}]$ centered on ρ_p)

$$\Psi^{JM}(\rho,\Omega) = \frac{1}{\rho^{5/2}}\sum_k \Phi_k^{JM}(\rho_p;\Omega) f_k^J(\rho_p;\rho) \tag{130}$$

coupled equations :

$$[-\frac{1}{2\mu}\frac{d^2}{d\rho^2} + \frac{15}{8\mu\rho^2} - E] f_k^J(\rho_p;\Omega) \; + \sum_{k'} H_{kk'}^J(\rho_p;\rho) \; f_k^J(\rho_p;\rho) = 0 \tag{131}$$

diabatic coupling terms:

$$H_{kk'}^J(\rho_p;\rho) = < \Phi_k^{JM}(\rho_p;\Omega)|H(p)|\Phi_{k'}^{JM}(\rho_p;\Omega) >_\Omega \tag{132}$$

diabatic couplings are smooth and well behaved, rapid variations of the non adiabatic P and Q couplings

Propagation inside a sector

– sector width : important parameter for the efficiency of the calculations

– small width : couplings (132) are almost diagonal (they are exactly diagonal for $\rho = \rho_p$)

– computational cost: if the basis functions is large, large number of diagonalizations is needed

– large sector width: decreases the computational cost of the basis, increases the one for the solution of the hyperradial equations (matrix elements (132) become large when p is far from the reference point ρ_p , more channels are necessary to represent the wavefunction with a given accuracy)

• several algorithms are currently in use for CC in inelastic scattering theory

• CC for the hyperradial equations (Johnson algorithm modified by Manolopoulos:

well suited to reactive problems, being both fast and accurate)

Propagation of the logarithmic derivative matrix:

$$\mathbf{Z}(\rho_p;\rho) = \mathbf{f}'(\rho_p;\rho)\mathbf{f}(\rho_p;\rho)^{-1} \tag{133}$$

from the left side $\rho_p^{(l)}$ to the right side $\rho_p^{(r)}$ of each sector

(133): $\mathbf{f}$ and $\mathbf{f}'$ are square matrices of order N (CC equations)

Propagation from one sector to the other

condition of continuity: $\rho^{5/2}\Psi^{JM}$ and of its ρ-derivative permits to relate the hyperradial components and derivatives at the left boundary of the sector centered on ρ_{p+1} to their values at the right boundary of the sector centered on ρ_p:

$$f_k(\rho_{p+1};\rho_{p+1}^{(l)}) = \sum_{k'} U_{kk'}(\rho_{p+1};\rho_p) f_k(\rho_p;\rho_p^{(r)}) \tag{134}$$

$$f'_k(\rho_{p+1};\rho_{p+1}^{(l)}) = \sum_{k'} U_{kk'}(\rho_{p+1};\rho_p) f'_k(\rho_p;\rho_p^{(r)}) \tag{135}$$

transformation matrix $\mathbf{U}(\rho_{p+1};\rho)$:

$$U_{kk'}(\rho_{p+1};\rho) = < \Phi_k^{JM}(\rho_p;\Omega)|\Phi_{k'}^{JM}(\rho_p;\Omega) > \tag{136}$$

(134) and (135) define starting conditions for integration of the coupled equations in sector $p+1$, transformation on the logarithmic derivative matrix $\mathbf{Z}$:

$$\mathbf{Z}(\rho_{p+1};\rho_{p+1}^{(l)}) = \mathbf{U}(\rho_{p+1};\rho_p)\mathbf{Z}(\rho_p;\rho_p^{(r)})U(\rho_{p+1};\rho_p)^{-1} \tag{137}$$

Asymptotic analysis

wavefunction Ψ^{JM} can be matched to the asymptotic form :

$$f^{J}_{\lambda' v' j' l' \lambda v j l}(R_{\lambda'}) \rightarrow f^{(1)}_{\lambda v j l}(R_\lambda)\delta_{\lambda'\lambda}\delta_{v'v}\delta_{j'j}\delta_{l'l} - f^{(2)}_{\lambda v j l}(R_{\lambda'})K^{J}_{\lambda' v' j' l' \lambda v j l} \tag{138}$$

for open channels:

$$f^{(1)}_{\lambda v j l}(R_\lambda) = k^{1/2}_{\lambda v j} R_\lambda j_l(k_{\lambda v j} R_\lambda) f^{(2)}_{\lambda v j l}(R_\lambda) = k^{1/2}_{\lambda v j} R_\lambda n_l(k_{\lambda v j} R_\lambda) \tag{139}$$

for closed channels: ($h^{(\pm)}_l$ are spherical Hankel functions)

$$\begin{aligned} f^{(1)}_{\lambda v j l}(R_\lambda) &= |k_{\lambda v j}|^{1/2} R_\lambda h^{(-)}_l(i|k_{\lambda v j}|R_\lambda) \\ f^{(2)}_{\lambda v j l}(R_\lambda) &= |k_{\lambda v j}|^{1/2} R_\lambda h^{(+)}_l(i|k_{\lambda v j}|R_\lambda) \end{aligned} \tag{140}$$

– on an hypersphere of radius $\rho_{\max}$, the quantity $\rho^{5/2}\Psi^{JM}$ and its ρ-derivative are continuous (the left and right values at $\rho = \rho_{\max}$ are the same for all Ω). One can thus project the continuity equations onto the basis functions of the last sector ρ_q whose right boundary $\rho_q^{(r)} = \rho_{\max}$

matrix of regular asymptotic solutions $\mathbf{f}^{(1)}$ and its derivative $\mathbf{f}^{(1)'}$:

$$f^{(1)J}_{k,\lambda vjl} =< \Phi^{JM}_k(\rho_p;\Omega)|\rho^{5/2}\Psi^{(1)JM}_{k,\lambda vjl}(\mathbf{R}_\lambda \mathbf{r}_\lambda) >_\Omega \tag{141}$$

$$(f^{(1)J}_{k,\lambda vjl})' =< \Phi^{JM}_k(\rho_p;\Omega)|\frac{\partial}{\partial\rho}(\rho^{5/2}\Psi^{(1)JM}_{k,\lambda vjl}(\mathbf{R}_\lambda \mathbf{r}_\lambda)) >_\Omega \tag{142}$$

$\Psi^{(1)JM}_{k,\lambda vjl}$ is the full regular asymptotic function:

$$\Psi^{(1)JM}_{k,\lambda vjl} \equiv \frac{1}{R_\lambda} f^{(1)}_{k,\lambda vjl}(R_\lambda)\Phi^{JM}_{k,\lambda vjl}(\widehat{\mathbf{R}}_\lambda \mathbf{r}_\lambda) \tag{143}$$

– quantities inside the ket in (141) and (142) are evaluated at $\rho = \rho_{\max}$

– matching equations are obtained from the condition that the numerically integrated logarithmic derivative matrix $\mathbf{Z}$ is equal to its asymptotic form

– imposing K- matrix boundary conditions:

$$\mathbf{Z} = (\mathbf{f}^{(1)\prime} - \mathbf{f}^{(2)\prime}\mathbf{K})(\mathbf{f}^{(1)} - \mathbf{f}^{(2)}\mathbf{K})^{-1} \tag{144}$$

– K-matrix, S-matrix:

$$\mathbf{K} = (\mathbf{Z}\mathbf{f}^{(2)} - \mathbf{f}^{(2)'})^{-1}(\mathbf{Z}\mathbf{f}^{(1)} - \mathbf{f}^{(1)\prime}) \tag{145}$$

$$\mathbf{S} = (\mathbf{1} + i\mathbf{K})/(\mathbf{1} - i\mathbf{K})^{-1} \tag{146}$$

A remark on flux conservation

traditional inelastic scattering theory:

- one shows that the logarithmic derivative matrix $\mathbf{Z}$ is a symmetric matrix, because of the symmetry of coupling matrices
- wronskian of asymptotic functions is unity
- K-matrix is symmetric
- S-matrix is symmetric and unitary

in reactive collisions:

- symmetry of the logarithmic derivative matrix is destroyed by the transformation (137), because $\mathbf{U}^{-1} \neq \mathbf{U}^{t}$

- Wronskian of the asymptotic solution matrices $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$ is not a unit matrix
- the K-matrix is no longer symmetric
- S-matrix is no longer unitary

in practice:
if enough closed channels are included in the wavefunction expansion, symmetry of the logarithmic derivative and K-matrices is preserved, at least for their open part

Hyperspherical coordinate systems

several choices for the five Ω hyperangles are possible:

- the generalization of spherical coordinates in three-dimensional space to six-dimensional space yields the following parametrization : $x_1 = \rho\cos\theta_1,\ x_2 = \rho\sin\theta_1\rho\cos\theta_2$,..., $x_5 = \rho\sin\theta_1\rho\sin\theta_2..\cos\theta_5,\ x_6 = \rho\sin\theta_1\rho\sin\theta_2..\sin\theta_5$ in which the hyperangles $\theta_1, ..., \theta_4$ lie between 0 and π and θ_5 lies between 0 and 2π

- this parametrization however suffers from the defect that the transformation of hyperangles when one performs a spatial rotation is complicated

- this implies that the potential energy V will depend on the five hyperangles in a manner which does not show rotational invariance explicitly and renders the calculation of matrix elements and of other quantities difficult

- in practice, to take account of rotational invariance and to simplify the

calculation of matrix elements, one has to use $body\text{-}frame$ coordinates in which three parameters (ρ and two hyperangles) specify the size and shape of the ABC triangle, while three Euler angles specify its orientation in space **Fock coordinates**

$(\rho, \omega_\lambda, \widehat{\mathbf{r}_\lambda}, \widehat{\mathbf{R}_\lambda})$: $\omega_\lambda = \arctan(r_\lambda / R_\lambda)$ lies between 0 and $\pi/2$

body-frame Fock internal coordinates $(\rho, \omega_\lambda, \eta_\lambda)$: η_λ is the angle between the two Jacobi vectors $\mathbf{r}_\lambda$ and $\mathbf{R}_\lambda$ and three Euler angle which specify the orientation of the molecular plane in space

the z axis of the molecular frame can be chosen to lie along $\mathbf{R}_\lambda$

there are of course three kinds of Fock coordinates, depending on the arrangement $\lambda = \alpha, \beta, \gamma$

Smith-Whitten democratic coordinates

the principal axis frame (the one in which the inertia tensor is diagonal):

– z-axis of the molecular frame to lie along the axis of least inertia

– y-axis: to be perpendicular to the molecular plane

– two angles Θ and Φ_λ : permit to compute the coordinates of the two Jacobi vectors in the molecular plane

$$Z_\lambda = \rho \cos\Theta \cos\Phi_\lambda, \quad z_\lambda = \rho \cos\Theta \sin\Phi_\lambda \tag{147}$$

$$X_\lambda = \rho \sin\Theta \sin\Phi_\lambda, \quad x_\lambda = -\rho \sin\Theta \cos\Phi_\lambda \tag{148}$$

– Θ: between 0 and $\pi/4$, Φ_λ : 0 and 2π

– moments of inertia:

$$I_z = \mu\rho^2 \sin^2\Theta \quad I_x = \mu\rho^2 \cos^2\Theta \quad I_y = \mu\rho^2 \tag{149}$$

– fixed ρ and Θ : the extremity of the vectors $\mathbf{R}_\lambda$ and $\mathbf{r}_\lambda$ lie on an ellipse whose half-axes are ρcosΘ and ρsinΘ

– $\Theta = 0$: corresponds to linear configurations

– $\Theta = \pi/4$: the two Jacobi vectors are perpendicular and the system is in a symmetric top configuration $(I_x = I_z = I_y/2)$

– three equal masses: corresponds to an equilateral ABC triangle, while, for a symmetric light-heavy-light system, we have a triangle with a right angle and two equal sides

– transformation (120): between the different sets of mass- weighted Jacobi

coordinates, one deduces easily that Smith-Whitten coordinates of arrangement β are the same as the ones of arrangement α, except for the angle Φ which changes as $\Phi_\beta = \Phi_\alpha - \Phi_{\alpha\beta}$

– Smith-Whitten coordinates of each arrangement are essentially the same, treat all particles on the same footing

Relation between Smith-Whitten and Fock coordinates

$$X_\alpha = \frac{\mathbf{R}_\alpha^2 - \mathbf{r}_\alpha^2}{\rho}, \quad Y_\alpha = \frac{\mathbf{R}_\alpha \mathbf{r}_\alpha}{\rho}, \quad Z = \frac{2R_\alpha r_\alpha \sin\eta_\alpha}{\rho}, S = \frac{1}{2}|\mathbf{R}_\alpha \times \mathbf{r}_\alpha| \qquad (150)$$

$X_\alpha^2 + Y_\alpha^2 + Z^2 = \rho^2$ can also be written as $4S/p$

S: surface of the mass-scaled triangle (and also of the real triangle ABC), invariant with respect to the arrangements

– with these coordinates, we can associate to each possible triangle shape and size a point in a 3D space:

- this permits a convenient mapping of potential surfaces
- the transf. between $(X_\alpha Y_\alpha Z)$ and $(X_\beta Y_\beta Z)$ is a rotation of angle $2\Phi_{\alpha\beta}$

- the expression of these coordinates in terms of Fock coordinates :

$$X_\alpha = \rho \cos 2\omega_\alpha, Y_\alpha = \rho \sin 2\omega_\alpha \cos \eta_\alpha, Z = \rho \sin 2\omega_\alpha \sin \eta_\alpha \tag{151}$$

- terms of Smith-Whitten coordinates

$$X_\alpha = \rho \cos 2\Theta \cos \Phi\alpha, Y_\alpha = \rho \cos 2\Theta \sin 2\Phi_\alpha, Z = \rho \sin 2\Theta \tag{152}$$

(151): apparent that $2\omega_\alpha$ and η_α are the (θ, ϕ) spherical angles in the $(Y_\alpha Z X_\alpha)$ system

(152): we see that $\pi/2$ - 2Θ and $2\Phi_\alpha$ are the (θ, ϕ) spherical angles in the $(Y_\alpha X_\alpha Z)$ system

Computer implementation and applications

- several implementations of the hyperspherical method exist at present
- it appears that Smith-Whitten coordinates are very convenient because they single out the projection of the total angular momentum onto the axis of least inertia
- this axis is close to the atom-diatom axis in each arrangement and rotates slowly from the reactant atom-diatom axis to the product one for reactions in which symmetric top configuration is not accessibler
- when quantizing internal motion onto this axis, one finds that rotational coupling is minimal for reactions in which the saddle point is in a linear or near-linear configuration

- the most expensive part of the computations lies in the solution of the close-coupling equations for all J and E values which are needed to get converged cross sections

- computer time scales as N^3 (N is the number of channels) matrix inversions

- using present day computers, systems involving about one thousand channels (or even more) can be treated and converged reaction cross sections have been recently obtained on systems like H + H_2 F +H_2 , Cl + H_2 and He +H_2^+, etc.

II.4 Recent developments, reduced dimensionality, negative imaginary potentials, etc.

see the volumes of: Bowman 1994, Zhang and Wyatt 1996, Baer 1986, etc.

Different variational principles

Authors: Truhlar; Kouri : Newton variational principle, Schwinger variational principle, amplitude density method, etc.

Authors: Miller, Zhang; Manolopolous, Wyatt : Kohn variational principle

Different body-fixed systems

Pack et al

Different hyperspherical approaches
Authors: Aquilanti , Lagana; Launay, Le Dourneuf: Linderberg; Pack, Parker,

Kress; Schatz; Manolopolous; Billing; Hinze, Wolniewiecz, Ahlijah

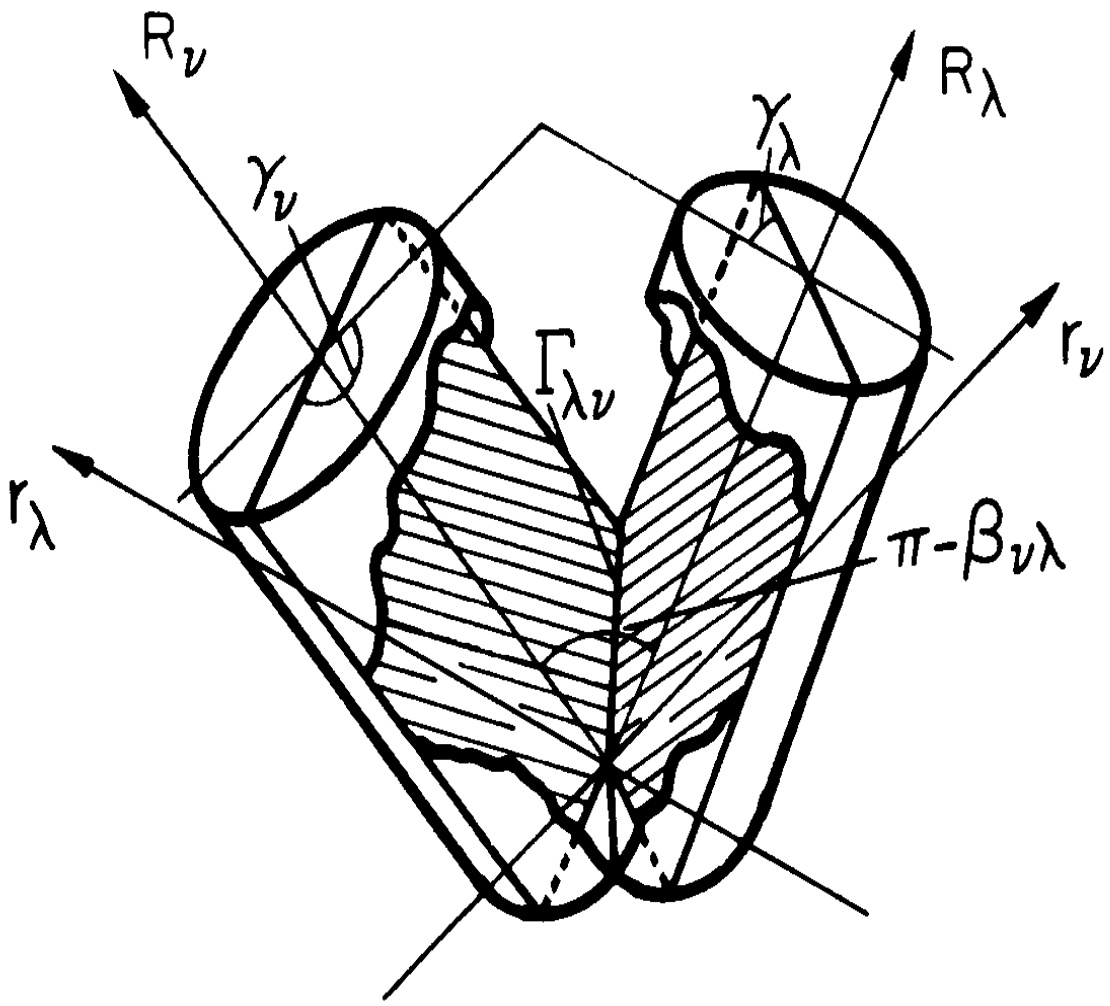
Different arrangement channel procedures
Authors: Kouri, Truhlar; Micha; Tang

Integral equation approaches
Authors: Kouri, Truhlar; Micha;

Time-independent wave packets
Authors: Kouri; Zhang; Althorpe et al

Approximate methods
Angular momentum decoupling
reactive infinite order sudden (RIOS) and other methods:CS, ES, etc.
Authors: Kouri; Pack; Jellinek; Baer;

Figure 3: RIOS: The λi- and ν- arrangement channels in cylindrical coordinates. The fixed γ_λ and γ_ν planes as well the borderline $\Gamma_{\lambda\nu}$ are shown.Jellinek et al in [1]



Faddeev approach
Author: Micha

T-matrix approach
Author: Tang

Distorted wave Born approximation
Authors: Schatz; Miller;Tang

Reduced dimensionality
Authors: Bowman; Clary; Hayes, Walker (bending-corrected rotating linear model); *Energy shift approximation*
Author: Bowman

Negative imaginary potentials
Authors: Last, Baer

Figure 4: Potential with a schematic wave function. (a) Without negative imaginary potential, (b) with negative imaginary potential. Collinear potential energ with NIP Last and Baer in [4]

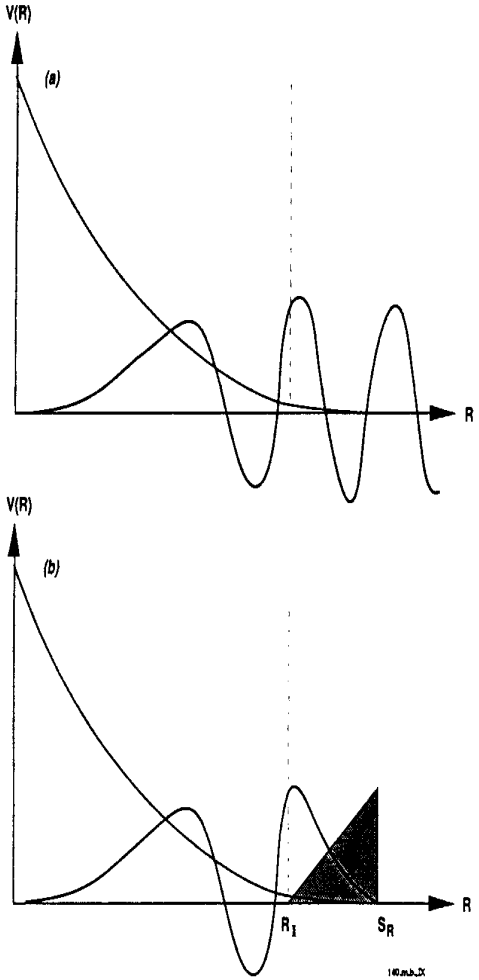
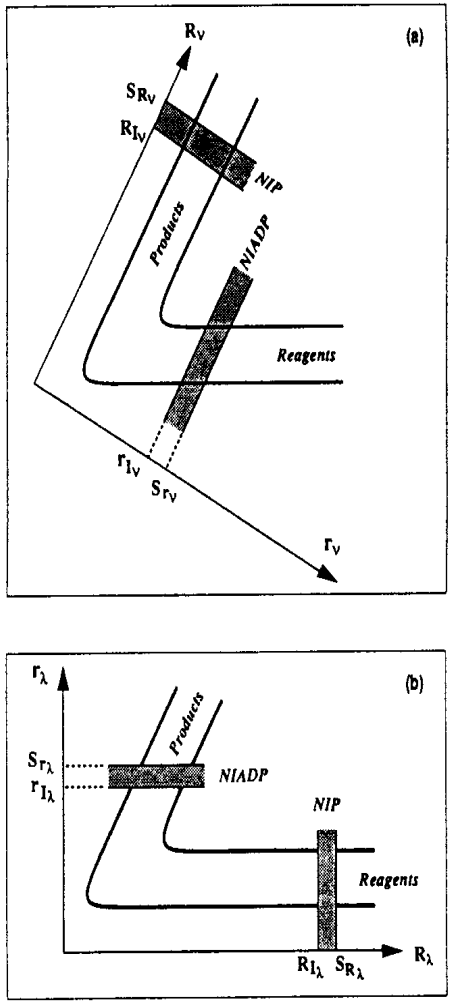


Figure 5: Collinear potential energ with NIP and NIADP. (a) product arrangement channel, (b) reagent arrangement channel. NIP: negative imaginary potential, NIADP: negative imaginary potential decoupling potential. Last and Baer in [4]



Four- and polyatomic reactions
Authors: Bowman; Clary; Schatz

Non-adiabatic reactions
Authors: Schatz, Connor; Baer; Truhlar; Nakamura

The geometric phase effect
Authors: Kupperman; Baer

II.5 Computer implementations and methodologies

Basis sets, DVR, FEM, etc.

see volumes of Lagana 1988, Cerjan 1993; [320], [8], [9]

The finite element method (FEM)

general idea of FEM:

- change from the integration to a summation over many subdomains called elements

- on each element the wavefunction is approximated by a parametrized function u

- simplest choice are polynomials of different degrees, e.g. in two dimensions

$$u(x,y) = \sum_{i,j} c_{ij} x^i y^j \tag{153}$$

- on each element e a certain number of grid points is choosen and the function

u on the element is expanded as

$$u^{(e)}(x,y) = \sum_{i=1}^{p} u_i^{(e)} \tilde{N}_i^{(e)}(x,y) = \sum_{i=1}^{p} u_i^{(e)} N_i^{(e)}(\zeta_1, \zeta_2, \zeta_3)$$

$$u_i^{(e)} = u(x_i, y_i) \tag{154}$$

- formfunctions $\tilde{N}_i^{(e)}$ $(N_i^{(e)})$ are defined to have interpolating properties inside each element e and are zero or one at the grid points:

$$\tilde{N}_i^{(e)}(x_j, y_j) = \delta_{ij} \tag{155}$$

- integrals over the whole domain of the problem are then sums over all elements
- we choose a triangular form of the elements

- simple integration formula, if one transforms from an arbitrary triangle to a unit rectangular triangle with the coordinates ξ and η and then to "natural triangular coordinates" ζ_i:

$$\begin{aligned} x &= x_1 + (x_2 - x_1)\xi + (x_3 - x_1)\eta \\ y &= y_1 + (y_2 - y_1)\xi + (y_3 - y_1)\eta \end{aligned} \tag{156}$$

$$\zeta_1 = 1 - \xi - \eta, \quad \zeta_2 = \xi, \quad \zeta_3 = \eta \tag{157}$$

- formfunctions can then be expressed in terms of the ζ_i

- general formulas in one and two dimensions

Grid schemes in FE for calculating a potential adapted basis.

reduction of computing time:

- we tested eigenfunctions that cover some or all different reaction channels and these eigenfunctions will build up an effective basis set for scattering

- this will be even more interesting for polyatomic systems if for each channel, potential adapted eigenfunctions (in more than one dimension) can be made available

- the problem that one has to deal with is the linear dependency

- we tested it for collinear $H + H_2$

- the most appropriate version is to include the complete area for the whole reaction including the break up into the three atoms

- the advantage of FE is to have the choice to use an irregular grid that is adapted to the given problem

- in our applications we normally use an equidistantly subdivided grid for that part of the potential area that is needed to describe the physics correctly

- within the multigrid methods the solution algorithm defines where to choose more grid points

- special grid for a special single solution

Aim: adapted grid that is nearly optimal for many solutions, e.g. many bound state wavefunctions or for scattering calculations with many collision energies

earlier work:
use of the Bohr-Sommerfeld (BS) formula to create a 1D grid that leads to a small number of points for which many eigenvalues (up to E_{max}) can be calculated

with the same high accuracy

grid points x_i: $\int_{x_{i-1}}^{x_i} p(x)dx \approx \pi\hbar$ with $p(x) = \sqrt{2\mu_x(E_{max} - V(x)}$ as the classical momentum corresponding to the energy E_{max}

now:
optimisation of the grid in 2D in two different ways depending on the underlying potential energy surface (PES)

first version:
– the grid depends on the contour lines of the PES for well choosen energy values

– each contour line is described by a number of points which are used for triangulation

– the energy values and the spacing of the points on the contour lines are

defined by some rules, e.g. logarithmic or exponential spacing for the energy values depending on the problem and enlarged spacing on the contour lines for high energies, e.g. well above the collision energy (Fig. 6)

– the triangulation should not create triangles with too sharp angles and not to many triangles have to be connected in one point (around 6 would be optimal), otherwise the polynomial approximation in FEM becomes numerically problematic

– depends on the number of grid points to start with and how dense they are lying

– beginning with the points of the contour lines, triangles are created and after that a reduction of triangles will proceed

– automatic grid generation is still not optimal

second version:

– using the BS-formula as in 1D

– starting with a relatively fine equidistant grid in 2D (e.g. in x,y (r and R in Jacobi coordinates)) we use the 1D formula for each stripe in x for a given y and vice versa for y for a given x values

– keep only those points that fulfil the requirements that the application of the 1D BS-formula leads to a solution in x- and y-direction

– advantage:
we do not create too many points for the grid mesh

the angles of the triangles are not too small

and practically no reduction of grid points has to be performed

Combination of FE and DVR

– ABC-systems: three coordinates (Euler angles are integrated out analytically), which are coupled more or less

– for Jacobi coordinates R, r, γ at least in the reactant channel R and r are more strongly coupled, so we solve the (R, r)- problem with FE (no separation Ansatz) and describe the angular part by a discrete variable representation (DVR)

– potential is expanded in Legendre polynomials, so for each fixed angle γ a 2D solution using FE is performed

Figure 6: $H + H_2$ [287], **a-c):** Three different discretizations for the angles $0^o, 45^o$ and 90^o are shown $(r, R = [0, 8]\ a_0)$. The discretization is based on a contour plot of the potential with energies $E =$ 0.12, 0.05, 0.02, 0.007 $a.u.$. **d)** A contour plot for 90^o is shown. During the triangulation process some contours were discarded.

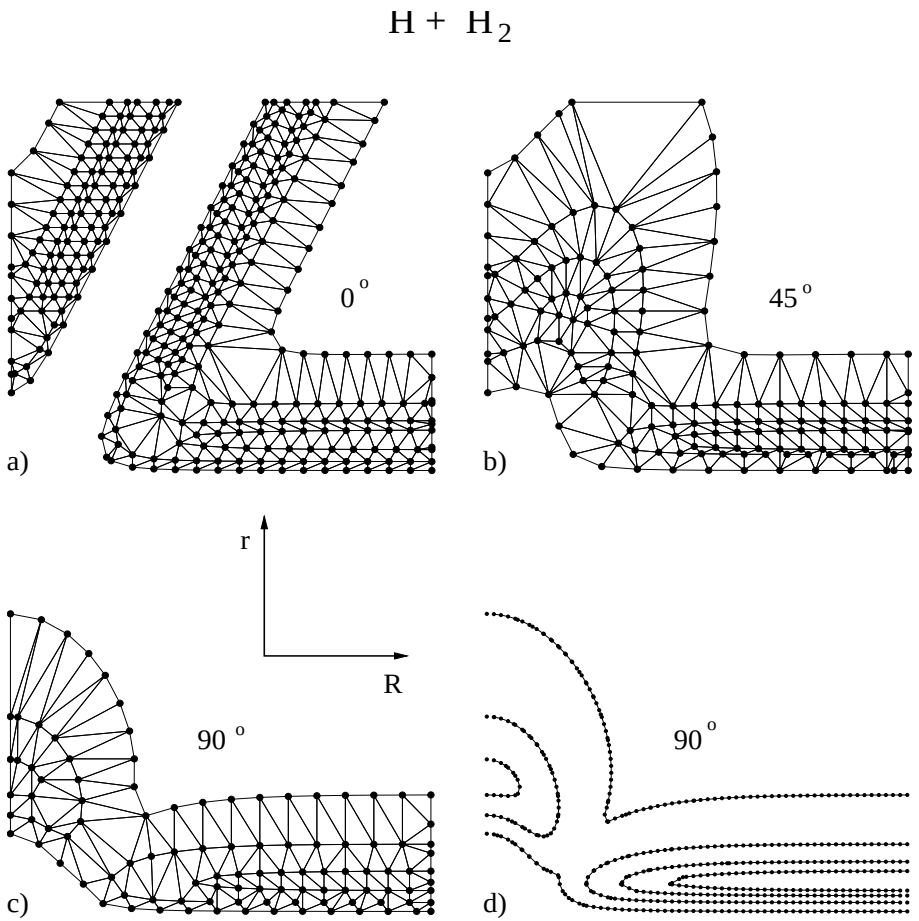


Figure 7: $H^+ + H_2$ [292], **a-c):** Three different discretizations for the angles $0^o, 45^o$ and 90^o are shown ($r, R = [0, 8]\ a_0$). The discretization is based on a contour plot of the potential with energies $E =$ 0.3, 0.23, 0.2, 0.187, 0.12, 0.09, 0.046, 0.004 $a.u.$. The first four energies match those of the H $+$ H_2 potential. **d)** A contour plot for 90^o is shown. During the triangulation process some contours were discarded.

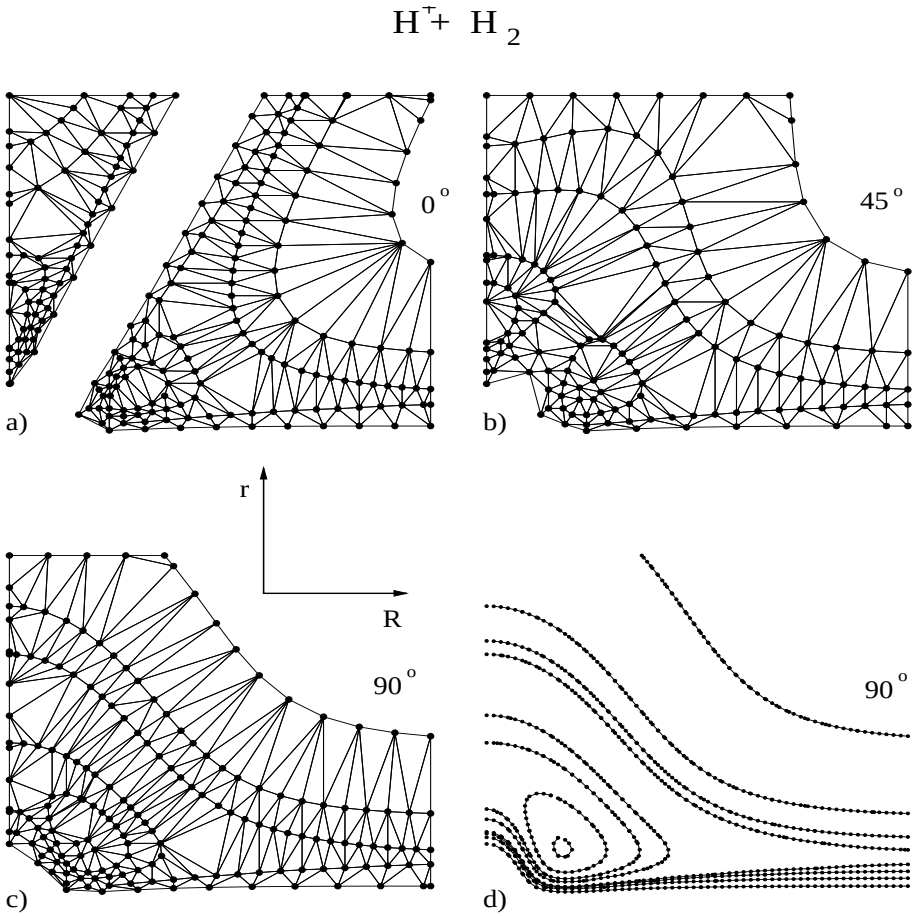
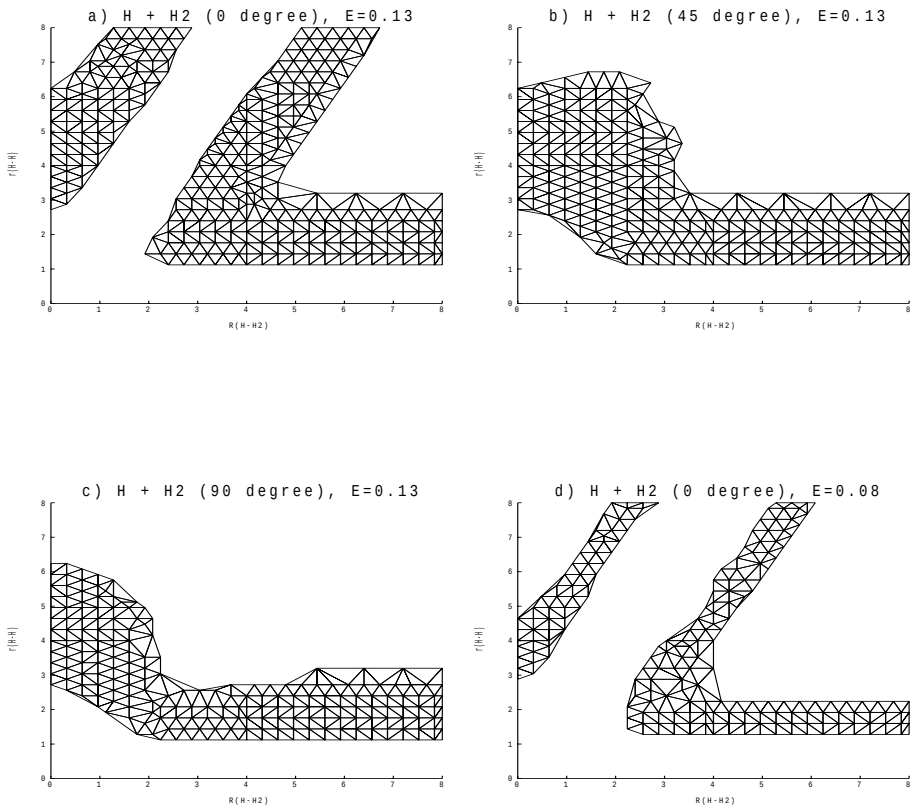


Figure 8: $H + H_2$ [287], **a-c):** Three different discretizations for the angles $0^o, 45^o$ and 90^o are shown $(r, R = [0, 8]\ a_0)$. The discretization is based on the combined use of the Bohr-Sommerfeld formula [20] in one dimension for r and R with $E_{max} = 0.13\ a.u.$. **d)** A smaller range for triangulation is shown for 0^o and with $E_{max} = 0.08\ a.u.$ (collinear arrangement).



Close coupling solvers

see volumes of Miller 1976, Bernstein 1979, etc.

Authors: Lester, Johnson, Manolopolous, Allison, Mrugala, Secrest, Thomas et al

R-matrix: Light et al, Trular et al

II.6 Examples: "Exact" calculations for H + H_2, F + H_2, etc.

Some remarks to Jacobi coordinates and scattering applications

Some remarks to hyperspherical coordinates and scattering applications

see the review of Manolopolous and Clary

H + H_2

see: reviews Truhlar, Miller, etc. (Adv. Phys. Chem.)

original work before 1980: Kuppermann et al, Wyatt et al, Light et al

List of potential energy surfaces for H + H_2:

PK, LSTH, DMBE, BKMP, BKMP2

New work on H + D_2:

see: Wrede, Welge et al

Figure 9: Selected v', j' state resolved DCSs in the CM system for the H + $D_2(v = 0mj = 0)$ $\rightarrow$ HD(v', j') + D reaction [360].

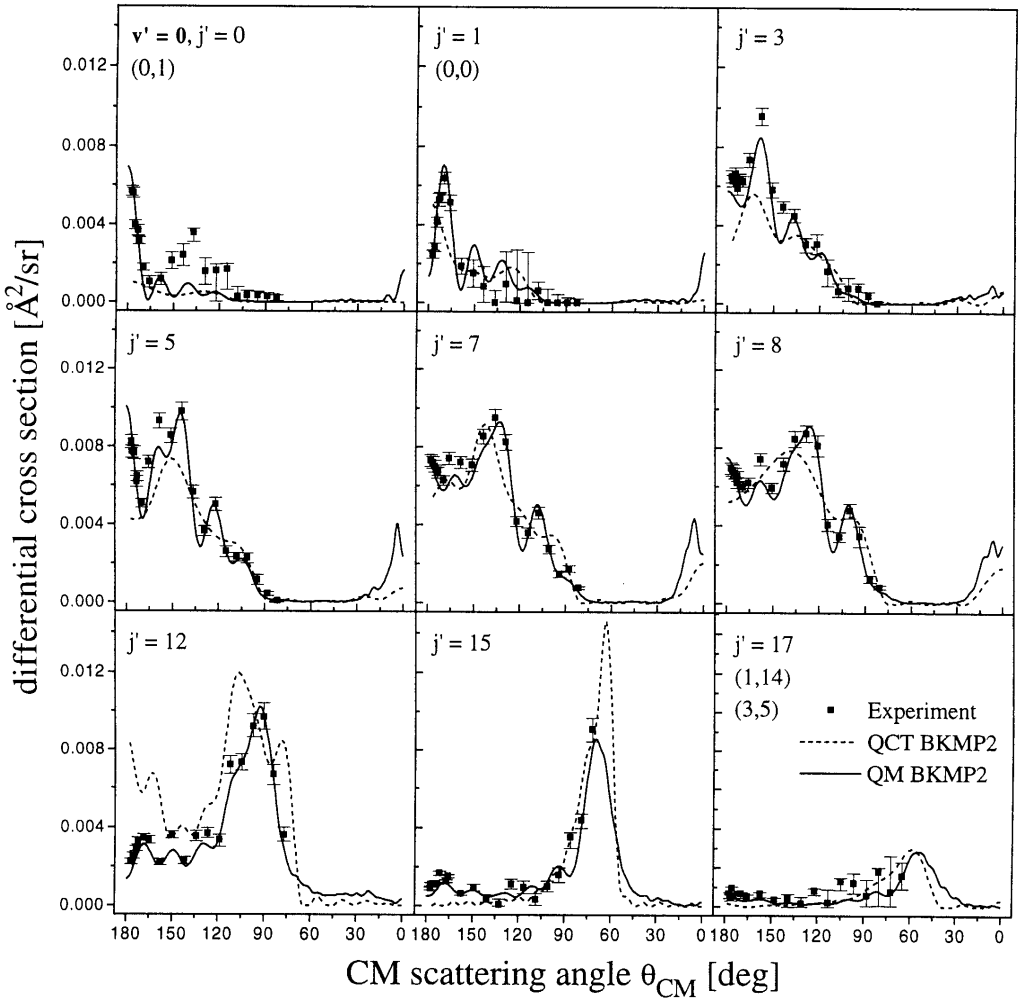
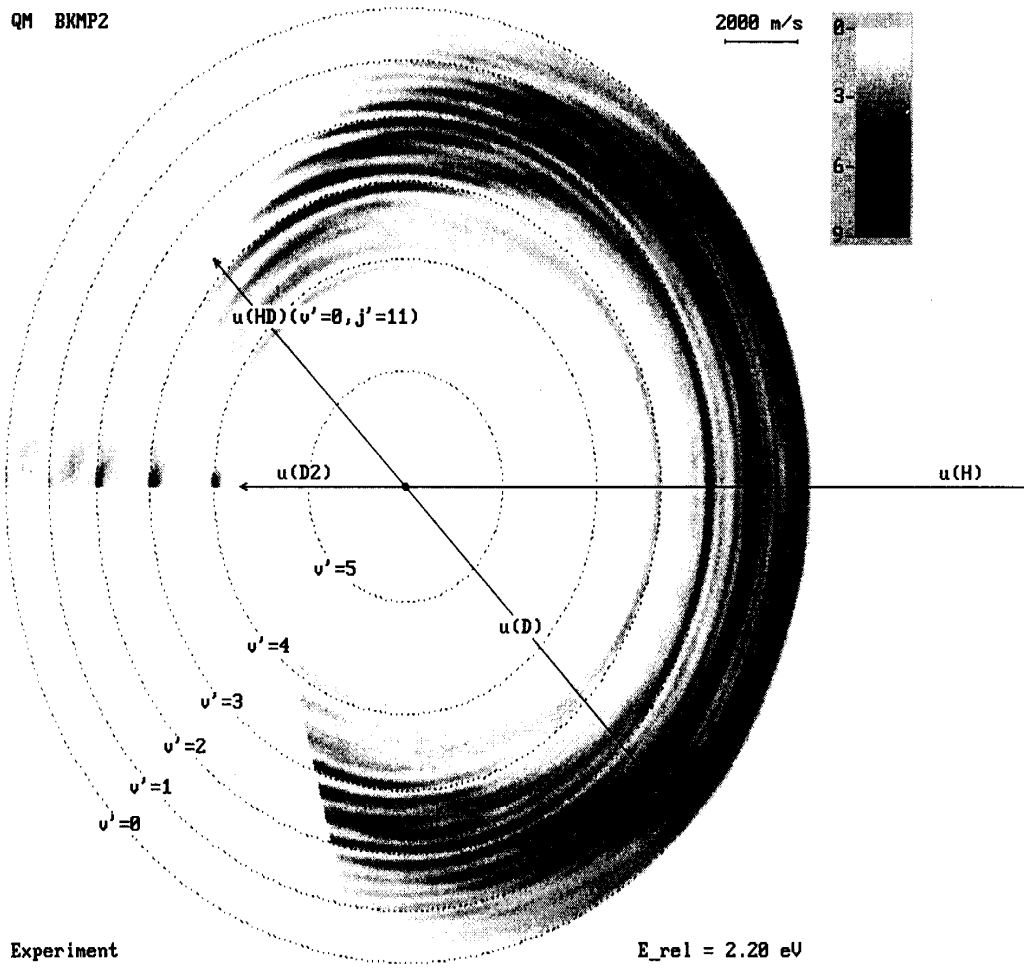


Figure 10: Composite D-atom angle velocity polar map of the H + $D_2(v = 0mj = 0)$ $\rightarrow$ HD + D reaction at 2.2 eV collision energy. The upper half has been constructed using the QM v', j' DCSs, whereas the lower half corresponds to the experimentally deduced DCSs [360].



Hyperspherical applications

$F + H_2$

see: Manolopolous et al

Figure 11: Quantum-mechanical LAB frame angular distributions for the F + HD(v=0,j=0) → DF(v') + H reaction at E_{coll}: (a) 1.35 and (b) 1.98 kcal mol^{-1}, compared with the results of the molecular beam experiment [322].

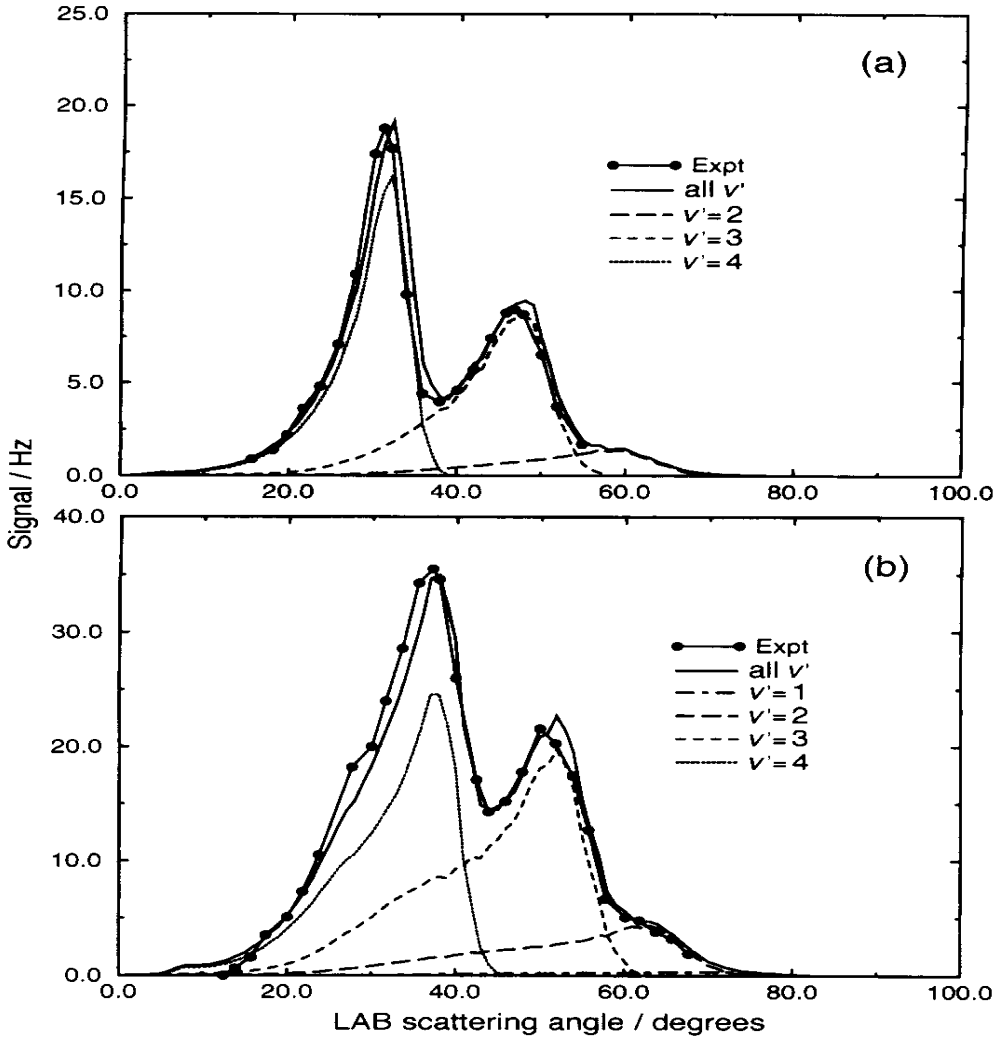
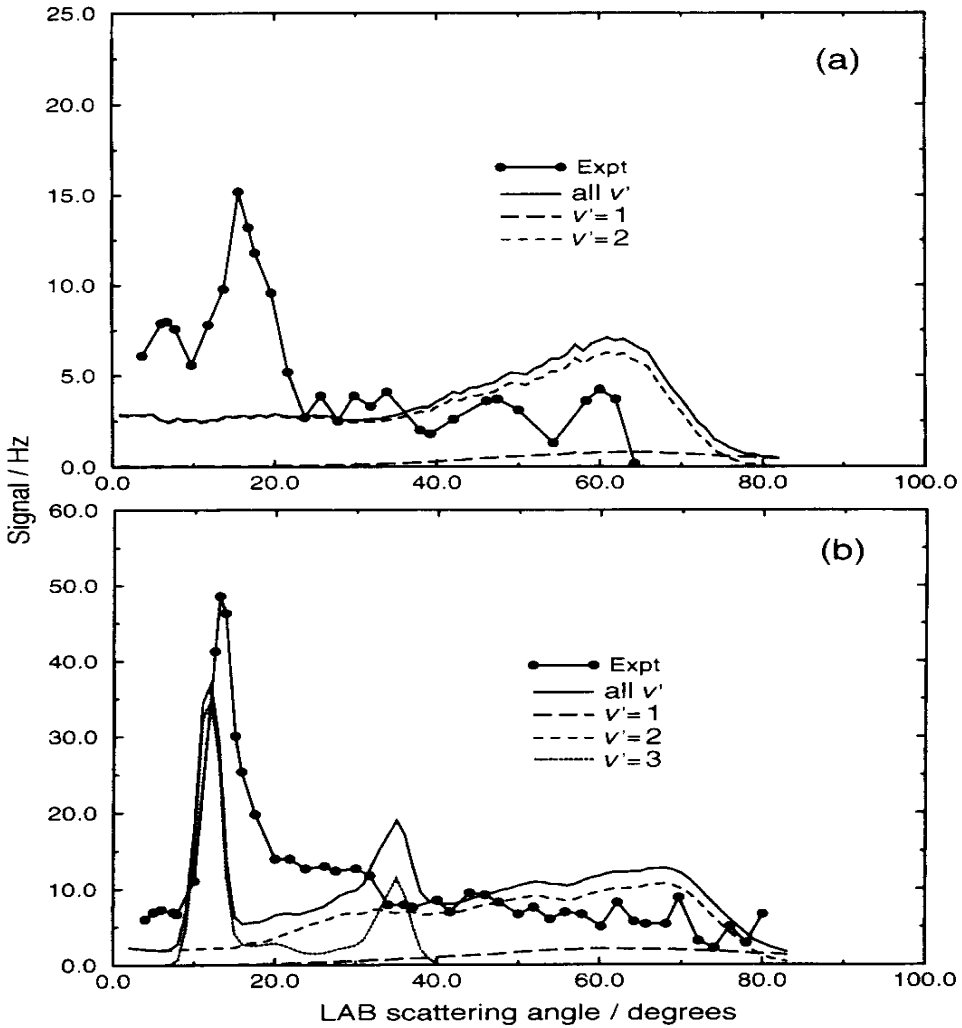


Figure 12: As in Fig. 11, but for F + HD(v=0,j=0) → HF(v') + D reaction [322].



The geometric phase effect in H + H_2

see: Kuppermann et al

Figure 13: Degeneracy- summed differential cross sections for the H + H_2 (v=0,j=0) $\rightarrow$ H_2 (v'=0,j'=2) +H reaction, at a total energy of 0.7 eV, as a function of scattering angle. From Ref. [335]

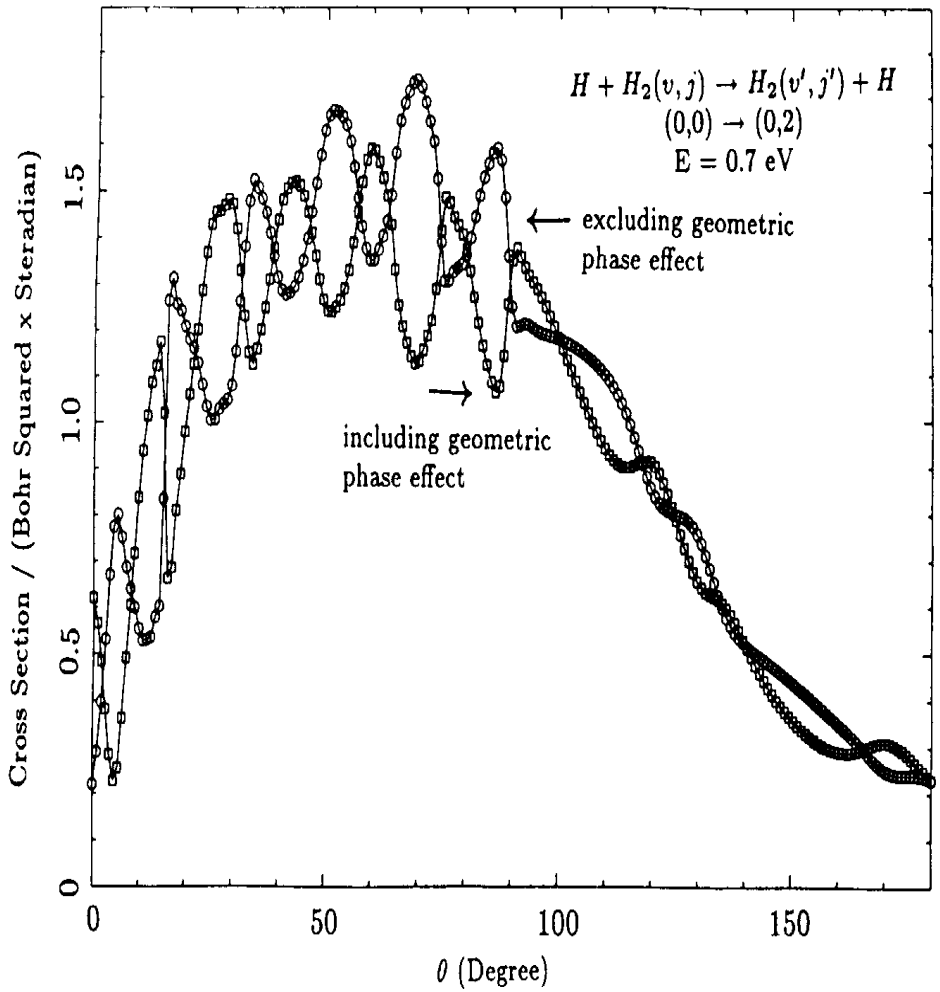


Figure 14: This figure depicts two kinds of semiclassical paths which contribute to exchange scattering amplitude for a triatomic system ABC. The dashed path partially encircles the conical intersection line, whereas the solid one does not. From Ref. [337]

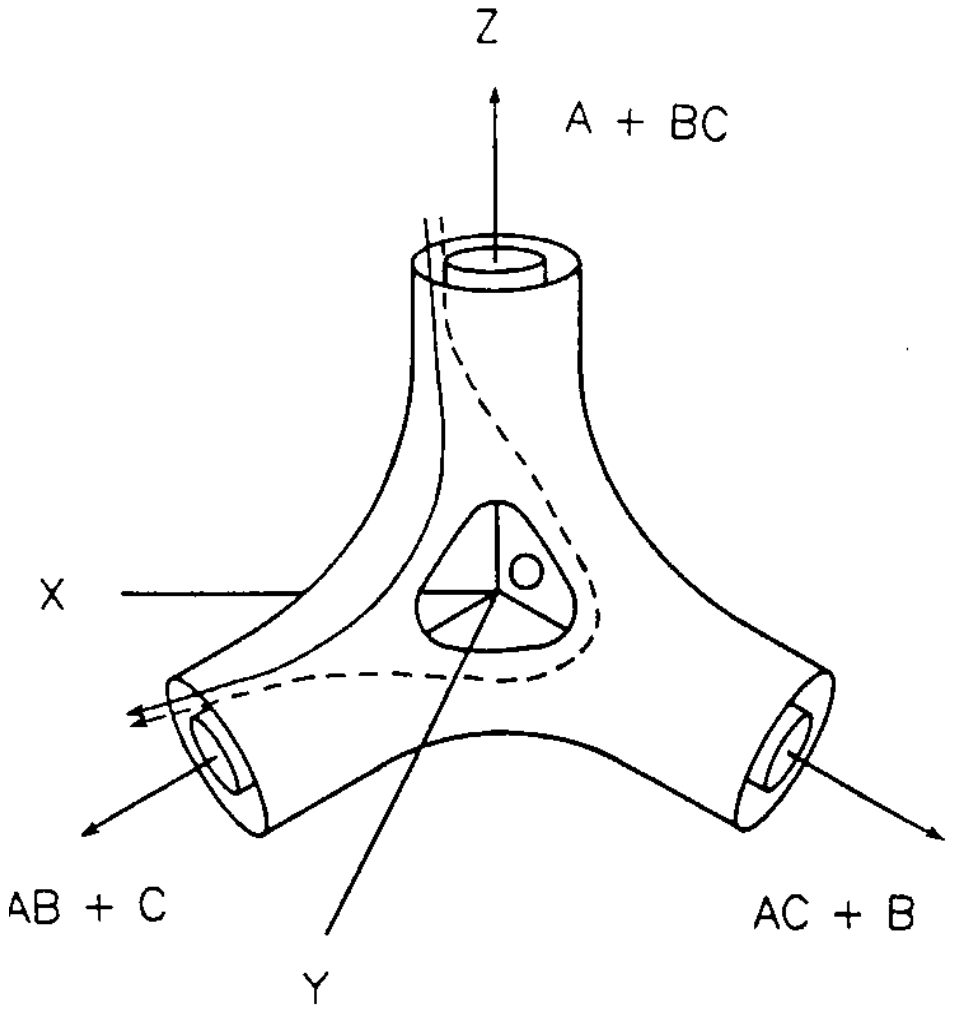
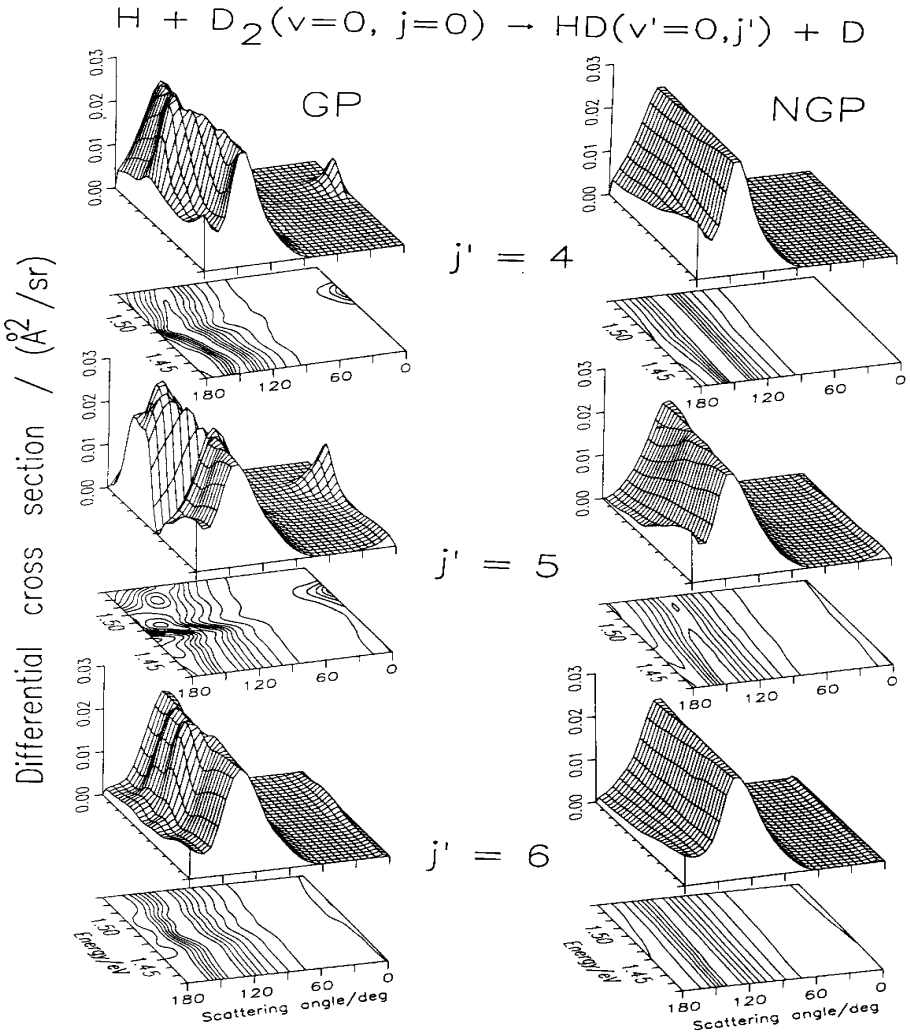


Figure 15: Degeneracy summed GP and GNP differential cross sections for the H + D_2 (v=0,j=0) $\rightarrow$ HD (v'=0,j') +D reaction as a function of total energy and of the center-of -mass scattering angle of the HD product. From Ref. [337]



Miscellaneous

different hyperspherical applications: see Nakamura

spin-orbit effects in reactions: Schatz et al

II.7 Summary

• variety of 'exact' ways to solve the SE for three dimensional atom-diatom reactions

• two leading approaches to quantum reactive scattering:

hyperspherical coordinate methods and variational methods

• based on the simultaneous use of mass-scaled Jacobi coordinates in each of the chemical arrangements involved

• the two approaches are somewhat complementary

• both have already seen numerous important applications

• it is as yet unclear which will ultimately prove the 'best' to use

hyperspherical coordinate methods (HCM) provide a physical picture of reactive scattering in terms of adiabatic hyperradial potential energy curves (AHPEC)

* AHPEC correlate asymptotically with the bound rovibrational energy levels of the reactant and product fragments

* HCM are useful for interpreting dynamical resonance effects

* HCM lead quite naturally to optimum angular momentum decoupling approximations of the coupled states or 'centrifugal sudden' form

Jacobi coordinate variational methods do not at present provide such a useful physical picture of the dynamics

* somewhat more amenable to perturbation theory approximations of the 'distorted wave' type

natural collision coordinate methods, which still give the most intuitive physical picture of all, appear to be computationally intractable for the more demanding reactions studied to date

- converged $J = 0$ and $J \neq 0$ reaction probabilities can now be obtained 'quite routinely' for a wide variety of atom-diatom reactions
- differential and integral cross sections can also be obtained at quite high scattering energies (e.g. for all the deuterium substituted analogues of H + H_2)
- cross sections for highly exoergic reactions with heavier atoms are still quite difficult to obtain
- a large number of experimentally interesting reactions fall into this latter category, the need for further methodological developments is clear

other important problems:

- study of electronically non-adiabatic reactions
- description of subtle geometric effects caused by the conical intersection of ground and excited electronic potential energy surfaces
- collision induced dissociation
- reactions involving polyatomic molecules
- **but**: potential energy surfaces and dynamics calculations appear at last to be converging on a realistic ab initio quantum theory of reactive scattering

II.8 Appendix

The body-fixed rotationally coupled Schrödinger equation

Separation of internal configuration space into arrangement channel regions

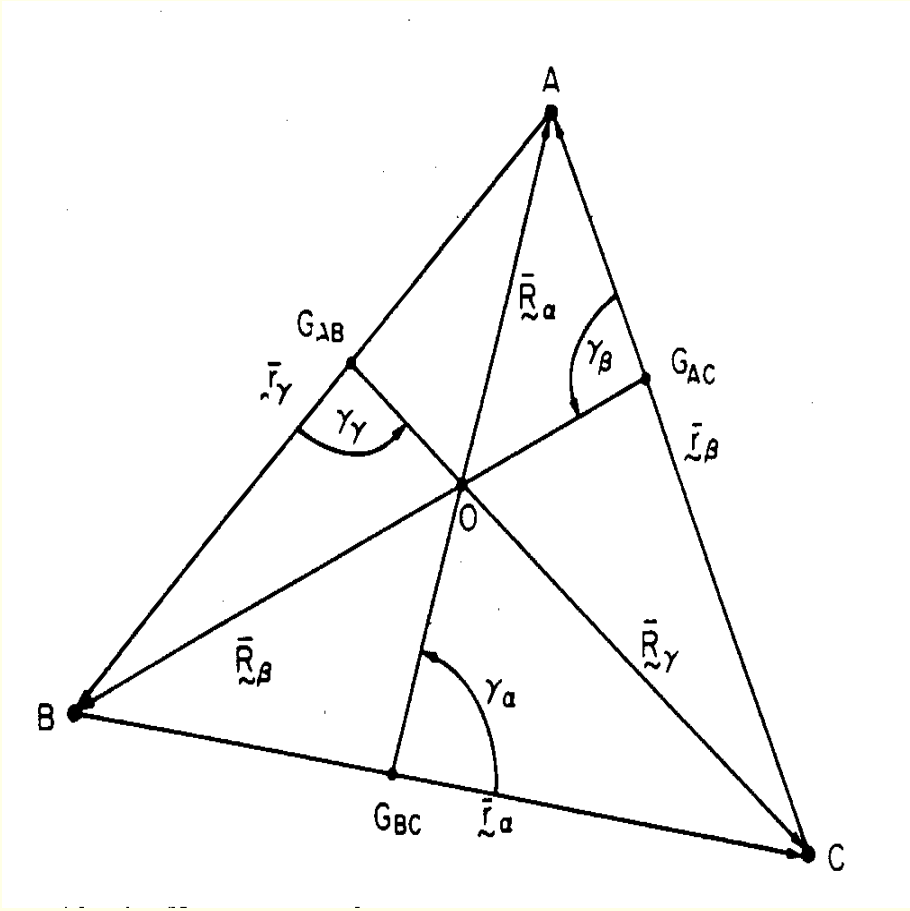


Figure 16: Vectors used to specify the location of the three atoms A, B, and C relative to the center of mass 0. G_{BC}, G_{AC}, and G_{AB} denote the locations of the centers of mass of the diatoms BC, AC, and AB, respectively.

- three-dimensional collision of an atom A with a diatomic molecule BC and, B plus CA and C plus AB collisions ($A(\equiv A_\alpha), B(\equiv A_\beta)$, $C(\equiv A_\gamma)$ Fig. 16

- $\bar{\mathbf{R}}_\alpha$: from the center of mass of BC to A, $\bar{\mathbf{r}}_\alpha$: from B to C, $|\bar{\mathbf{R}}_\alpha| \to \infty$ with $|\bar{\mathbf{r}}_\alpha|$ remaining finite: separated A+BC arrangement channel α

- the arrangement of the vectors in Fig. 16 is cyclic in the indices $\alpha\beta\gamma$; $\lambda\nu\mu$ represent any one of the cyclic permutations $\alpha\beta\gamma, \beta\gamma\alpha$ and $\gamma\alpha\beta$

- scaled variables $\mathbf{R}_\lambda, \mathbf{r}_\lambda$ are related to $\bar{\mathbf{R}_\lambda}, \bar{\mathbf{r}_\lambda}$ by:

$$\mathbf{r}_\lambda = a_\lambda^{-1} \bar{\mathbf{r}_\lambda} \tag{158}$$

$$\mathbf{R}_\lambda = a_\lambda \bar{\mathbf{r}_\lambda} \tag{159}$$

$$a_\lambda = (\mu_{\lambda,\nu k}/\mu_{\nu k})^{1/4} \tag{160}$$

$$\mu_{\lambda,\nu k} = m_\lambda(m_\nu + m_k)/(m_\lambda + m_\nu + m_k) \tag{161}$$

$$\mu_{\nu k} = m_\nu m_k/(m_\nu + m_k) \tag{162}$$

- convenient representation of the potential V with R_λ, r_λ and γ_λ ($\lambda = \alpha, \beta, \gamma$):

$$\gamma_\lambda = \cos^{-1} \frac{\mathbf{R}_\lambda \mathbf{r}_\lambda}{|\mathbf{R}_\lambda||\mathbf{r}_\lambda|} \quad 0 \leq \gamma_\lambda \leq \pi \tag{163}$$

- $V = V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$

- $\mathbf{R}_\lambda, \mathbf{r}_\lambda$, are useful for describing the triatomic motions only for configurations in which R_λ is significantly larger than, say, R_ν or R_k

- representation of V^{λ} in terms of variables $\xi = (r_{\lambda}^2 + R_{\lambda}^2)^{1/2}$, $\omega_{\lambda} = 2\tan^{-1}(r_{\lambda}/R_{\lambda})$ (in the 0 to π range), and γ_{λ}

- range of γ_{ν} in 3D: 0 to π, in 2D: 0 to 2π

- three-dimensional internal configuration space: divided into arrangement channel region subspaces $\lambda = \alpha, \beta, \gamma$

- in region λ (for large ξ) R_{λ} is approximately equal to Z_{λ} and r_{λ} is approximately half of the distance of the point $P(\xi, \omega_{\lambda}, \gamma_{\lambda})$ to the Z_{λ} axis

- in that region, $R_{\lambda}, r_{\lambda}, \gamma_{\lambda}$ are the "natural" variables for describing the translational, vibrational, and rotational motions of the three atoms, but these same variables are both awkward and inefficient for representing the corresponding motions in arrangement channels ν and k

- we (Kuppermann) use $R_{\lambda}, r_{\lambda}, \gamma_{\lambda}$ in region λ only

- three additional external variables (which specify the orientation of the instantaneous three-atom triangle with respect to a laboratory system) which will also be different for different arrangement channel regions

- Kuppermann: solving the SE involves first the generation of solutions in each of the three arrangement channel regions $\lambda = \alpha, \beta, \gamma$ in separate calculations using variables appropriate to each region

- followed by a matching procedure which yields a set of smooth and continuous solutions throughout all of configuration space

- then we (Kuppermann) need to linearly combine these "primitive" solutions to generate ones which satisfy the desired asymptotic boundary conditions

- choice of boundary surfaces for H + H_2: three half-planes $\pi_{\nu\lambda}, \pi_{k\nu}$ and $\pi_{\lambda k}$

- they are limited by and intersect on the OY_λ axis, $\pi_{\nu\lambda}$ makes an angle $\beta_{\nu\lambda}$ (in

the 0 to $\pi/2$ range) with the $OY_\lambda Z_\lambda$ plane:

$$\cos\beta_{\nu\lambda} = \left(\frac{m_\nu m_\lambda}{(m_\lambda + m_k)(m_\nu + m_k)}\right)^{1/2} \tag{164}$$

$$\sin\beta_{\nu\lambda} = \left(\frac{m_k M}{(m_\lambda + m_k)(m_\nu + m_k)}\right)^{1/2} \tag{165}$$

$$M = m_\lambda + m_\nu + m_k \tag{166}$$

analogous expressions are valid for the angles between $\pi_{k\nu}$ and $OY_\lambda Z_\nu$, and between $\pi_{\lambda k}$ and $OY_\lambda Z_k$

these $\pi_{\nu\lambda}$ surfaces ($\nu\lambda = \alpha\beta, \beta\gamma, \gamma\alpha$) are called the **matching surfaces**

Partial wave analysis

coordinates specified by the index λ: SE for the motions of the three nuclei

$$(-\frac{\hbar^2}{2\mu_{\lambda,\nu k}}\nabla^2_{\bar{\mathbf{R}_\lambda}} - \frac{\hbar^2}{2\mu_{\nu k}}\nabla^2_{\bar{\mathbf{r}_\lambda}} + V^\lambda(\bar{\mathbf{r}_\lambda}, \bar{\mathbf{R}_\lambda}, \gamma_\lambda) - E)\Psi^\lambda(\bar{\mathbf{r}_\lambda}, \bar{\mathbf{R}_\lambda}) = 0 \qquad (167)$$

scaled coordinates:

$$(-\frac{\hbar^2}{2\mu}(\nabla^2_{\bar{\mathbf{R}_\lambda}} + \nabla^2_{\bar{\mathbf{r}_\lambda}}) + V^\lambda(\mathbf{r}_\lambda, \mathbf{R}_\lambda, \gamma_\lambda) - E)\Psi^\lambda(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = 0 \qquad (168)$$

$$\mu = (\mu_{\lambda,\nu\chi}\mu_{\nu\chi})^{1/2} = [m_\lambda m_\nu m_\chi/(m_\lambda + m_\nu + m_\chi)]^{1/2} \qquad (169)$$

μ is independent of the choice of arrangement channel

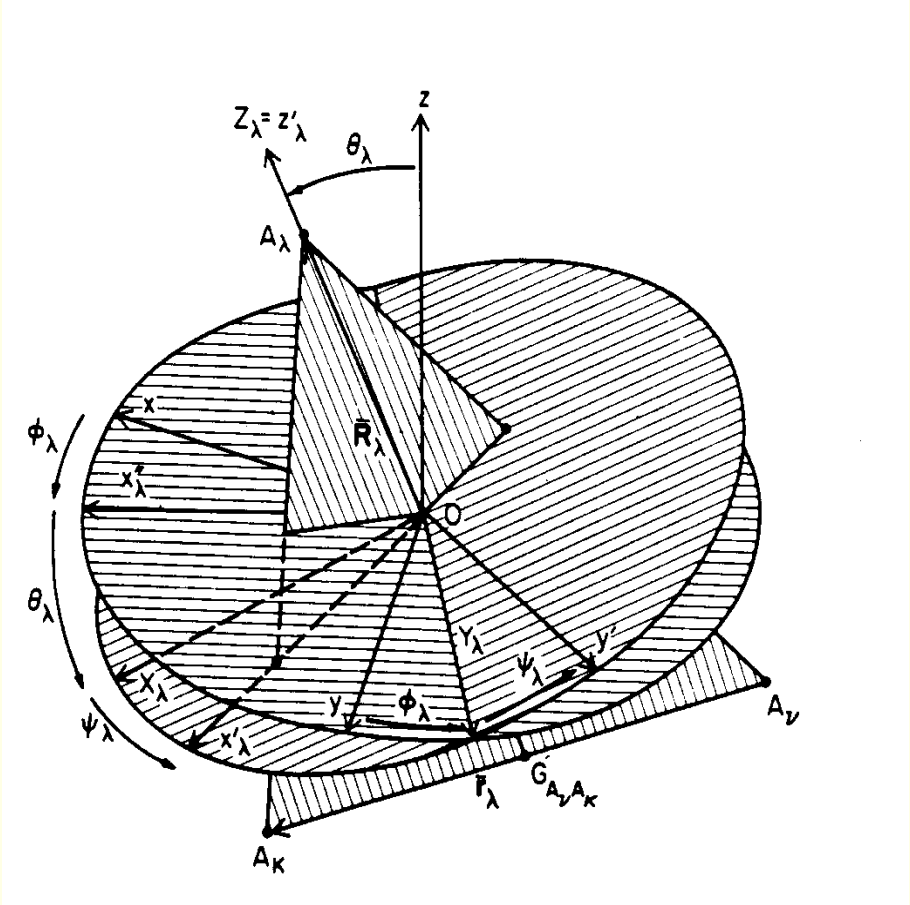


Figure 17: Space-fixed coordinate system Oxyz and body-fixed systems $OX_\lambda Y_\lambda Z_\lambda$ and $Ox'_\lambda y' z'_\lambda$. The origin O of this figure is the same as that of Fig. 16.

space fixed coordinate system $Oxyz$ (Fig. 17) centered on the center of mass O of the triatom system:

axes are constantly parallel to the axes of a laboratory-fixed system of coordinates, in $Oxyz$ the polar and azimuthal angles of $\mathbf{R}_\lambda$ and $\mathbf{r}_\lambda$ are $\theta_\lambda, \phi_\lambda$ and $\theta_{r_\lambda}, \phi_{r_\lambda}$

$$[-\frac{\hbar^2}{2\mu}(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda+\frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda)+\frac{j_\lambda^2}{2\mu r_\lambda^2}+\frac{l_\lambda^2}{2\mu R_\lambda^2}+V^\lambda(r_\lambda, R_\lambda-\lambda, \gamma_\lambda)-E]\Psi^\lambda(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = 0 \tag{170}$$

$\mathbf{l}_\lambda$ and $\mathbf{j}_\lambda$ usual orbital and rotational angular momentum operators expressed in the spherical coordinates $\theta_\lambda, \phi_\lambda$ and $\theta_{r_\lambda}, \phi_{r_\lambda}$

total angular momentum operator $\mathbf{J}$: independent of arrangement channel

$$\mathbf{J} = \mathbf{l}_\lambda + \mathbf{j}_\lambda \tag{171}$$

$\mathbf{J^2}$ and $\mathbf{J_z}$ (the z component of $\mathbf{J}$) commute with each other and with the Hamiltonian H

partial wave analysis procedure: expansion of $\Psi^\lambda(\mathbf{r}_\lambda, \mathbf{R}_\lambda)$ in terms of simultaneous eigenfunctions $\Psi^\lambda_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda)$ of J^2, J_z and H with eigenvalues $\hbar^2 J(J+1), \hbar M$ and E

$$\Psi^\lambda(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{J=0}^{\infty} \sum_{M=-J}^{J} C^\lambda_{JM} \Psi^\lambda_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) \tag{172}$$

$\Psi^\lambda_{JM}(r_\lambda, R_\lambda)$ satisfies170

The body-fixed Schrödinger equation

• standard space-fixed theory (Arthurs and Dalgarno) expansion of Ψ^{λ}_{JM} in terms of a set of simultaneous eigenfunctions of $\mathbf{J^2}, J_z, \mathbf{l}^2_\lambda$ and $\mathbf{j}^2_\lambda$ thereby obtaining a set of coupled equations in the quantum numbers j_λ and l_λ

• alternative: transformation to a system of body-fixed coordinates (Pack)

• fully converged calculation: body-fixed and space-fixed formalisms lead to the same number of coupled equations; for fully converged non-reactive atom diatom calculations, they may be implemented with comparable ease

• body-fixed coordinate systems lead to an approximate decoupling of certain degrees of freedom, which is not naturally present in the space-fixed analysis and which is useful in the development of approximate theories

• body-fixed analysis leads to both computational and conceptual simplifications

in the matching procedure, thus providing a considerable advantage in reactive scattering calculations over the corresponding space-fixed theory (calculations in the 1970ies)

- two body-fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ and $Ox'_\lambda y' z'_\lambda$ (see Fig. 17):

(1) $OX_\lambda Y_\lambda Z_\lambda$ is obtained from $Oxyz$ by rotating through the Euler angles $\alpha = \phi_\lambda, \beta = \theta_\lambda, \gamma = 0$ so that the Z_λ axis points along the R_λ direction and the Y_λ axis lies in the xy plane

(2) $Ox'_\lambda y' z'_\lambda$ is obtained from $OX_\lambda Y_\lambda Z_\lambda$ by rotating it counterclockwise about $OZ_\lambda (\equiv Oz'_\lambda)$ by an angle ψ_λ (in the 0 to π range) so as to bring Ox'_λ into the R_λ, r_λ plane and Oy' (which is independent of λ) perpendicular to it and oriented in the direction of $R_\lambda \times r_\lambda$:

$$\hat{\mathbf{y}}' = \frac{\mathbf{R}_\lambda \times \mathbf{r}_\lambda}{|\mathbf{R}_\lambda \times \mathbf{r}_\lambda|} \tag{173}$$

- Euler angles which rotate $Oxyz$ to $Ox'y'z'$ are $\alpha = \phi_\lambda, \beta = \theta_\lambda, \gamma = \psi_\lambda$

- in either of the body-fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ or $Ox'_\lambda y' z'_\lambda$ thevariables used to describe the system are $r_\lambda, R_\lambda, \phi_\lambda, \theta_\lambda, \psi_\lambda, \gamma_\lambda$

- ψ_λ is the counterclockwise angle from OY_λ to Oy' or from OX_λ to Ox'_λ as viewed from the positive OZ_λ axis

- OY_λ is perpendicular to the $OX_\lambda Z_\lambda$ plane and therefore the R_λ, Oz plane, and Oy' is perpendicular to the $\mathbf{R}_\lambda, \mathbf{r}_\lambda$ plane

- ψ_λ is the angle between these last two planes

- the plane containing the three axes OX_λ, Ox'_λ and OY_λ is perpendicular to the $\mathbf{R}_\lambda$ vector and intersects the $\mathbf{R}_\lambda, Oz$ and $\mathbf{R}_\lambda, \mathbf{r}_\lambda$planes along the OX_λ and Ox'_λ axes

• the angle ψ_λ between these two axes is equal to the angle between those two planes

• a motion, in which $R_\lambda, \phi_\lambda, \theta_\lambda, r_\lambda$ and γ_λ are kept constant but ψ_λ varies is a "tumbling" (i. e., rigid rotation) of the triatomic system around the $\mathbf{R}_\lambda$ vector, and for this reason the ψ_λ angle will be called the tumbling angle

• most convenient: use the coordinate system $OX_\lambda Y_\lambda Z_\lambda$ for deriving the coupled form of the SE and $Ox'y'z'$ in developing the matching procedure

expansion of Ψ^λ_{JM} in terms of the elements of the Wigner rotation matrix $\mathbf{D}(\alpha, \beta, \gamma)$:

$$\Psi^\lambda_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{\Omega_\lambda=-J}^{J} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0)\Psi^\lambda_{J\Omega_\lambda}(r_\lambda, R_\lambda, \gamma_\lambda, \psi_\lambda) \qquad (174)$$

$\Psi^{\lambda}_{J\Omega_\lambda}$: body-fixed wavefunction

quantum number Ω_λ:component of the total angular momentum $\mathbf{J}$ around $\mathbf{R}_\lambda$ or OZ_λ, $\mathbf{l}_\lambda$ (conjugate to R_λ) around this axis vanishes, Ω_λ specifies the Z_λ component of the angular momentum j_λ in the body-fixed frame

- J_{Z_λ} or $j_{\lambda z_\lambda}$ are the tumbling angular momentum (since it describes the tumbling of the triatom round $\mathbf{R}_\lambda$) and Ω_λ as the tumbling quantum number in arrangement channel λ

- substitution of 174 into 170 yields the following set of Ω_λ -coupled equations for the $\Psi^{\lambda}_{J\Omega_\lambda}(r_\lambda, R_\lambda, \gamma_\lambda, \psi_\lambda)$:

$$H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda}\Psi^{\lambda}_{J\Omega_\lambda} + H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda+1}\Psi^{\lambda}_{J,\Omega_\lambda+1} + H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda-1}\Psi^{\lambda}_{J\Omega_\lambda-1} = E\Psi^{\lambda}_{J\Omega_\lambda} \qquad (175)$$

$H^{J\lambda}_{\Omega_\lambda,\Omega'_\lambda}$: elements of a tridiagonal H-operator matrix $\mathbf{H}^{J\lambda}(r_\lambda, R_\lambda, \gamma_\lambda, \psi_\lambda)$

$$H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda} = -\frac{\hbar^2}{2\mu}(\frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda + \frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda) +$$

$$\frac{j_\lambda^2}{2\mu r_\lambda^2} + \frac{1}{2\mu R_\lambda^2}[J(J+1)\hbar^2 - 2\Omega_\lambda\hbar j_{\lambda z_\lambda} + j_\lambda^2] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) \qquad (176)$$

$$H^{J\lambda}_{\Omega_\lambda,\Omega_\lambda\pm1} = -\frac{\hbar}{2\mu R_\lambda^2}\sqrt{J(J+1) - \Omega_\lambda(\Omega_\lambda \pm 1)}j_\lambda^{\mp} \qquad (177)$$

$j_\lambda^{\mp}$: lowering (-) and raising $(+)$ operators of $\mathbf{j}_\lambda$ in-the body-fixed $OX_\lambda Y_\lambda Z_\lambda$ coordinate system

defining Ψ_J^λ as the $(2\Omega+1)$ dimensional column vector whose elements are the

$\Psi^{\lambda}_{J\Omega_\lambda}$, 175 can be put in the matrix form (body-fixed partial wave SE)

$$\mathbf{H}^{J\lambda}\Psi^{\lambda}_{J} = E\Psi^{\lambda}_{J} \tag{178}$$

kinetic energy operator is no longer diagonal in the body-fixed representation and is the mechanism which couples different quantum numbers Ω_λ

the potential coupling is diagonal in Ω_λ and is responsible for coupling between states of different vibration rotation quantum numbers v_λ, j_λ

this separation of kinematic and potential coupling is of prime importance in the development of approximate decoupling procedures

Table 1. Angular momentum operators in space-fixed and body-fixed coordinate systems [a]

$J_x =$	$-i\hbar(-\cos\phi\cot\theta\frac{\partial}{\partial\phi}$ $-\sin\phi\frac{\partial}{\partial\theta}+\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\psi})$	$J_{X_\lambda} =$	$-i\hbar(-\frac{1}{sin\theta}\frac{\partial}{\partial\phi}+\cos\theta\frac{\partial}{\partial\psi})$	$J_{x'\lambda} =$	$-i$ $+s$
$J_y =$	$-i\hbar(-\sin\phi\cot\theta\frac{\partial}{\partial\phi}$ $+\cos\phi\frac{\partial}{\partial\theta}+\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\psi})$	$J_{Y_\lambda} =$	$-i\hbar\frac{\partial}{\partial\theta}$	$J_{y'} =$	$-i$ $+c$
$J_z =$	$-i\hbar\frac{\partial}{\partial\phi}$	$J_{Z_\lambda} =$	$-i\hbar\frac{\partial}{\partial\psi}$	$J_{z'_\lambda} =$	$-i$
$j_{\lambda x} =$	$-i\hbar[\cos\phi\sin\theta+\sin\phi\sin\psi\cot\gamma$ $-\cos\phi\cos\theta\cos\psi\cot\gamma)\frac{\partial}{\partial\psi}$ $-(\sin\phi\cos\psi+\cos\phi\cos\theta\sin\psi)\frac{\partial}{\partial\gamma}]$	$j_{\lambda X_\lambda} =$	$-i\hbar(-\cos\psi\cot\gamma\frac{\partial}{\partial\psi}$ $-\sin\psi\frac{\partial}{\partial\gamma})$	$j_{\lambda x'_\lambda} =$	$-i$
$j_{\lambda y} =$	$-i\hbar[(\sin\phi\sin\theta-\cos\phi\sin\psi\cot\gamma$ $-\sin\phi\cos\theta\cos\psi\cot\gamma\frac{\partial}{\partial\psi}$ $+(\cos\phi\cos\psi-\sin\phi\cos\theta\sin\psi)\frac{\partial}{\partial\gamma}]$	$j_{\lambda Y_\lambda} =$	$-i\hbar(-\sin\psi\cot\gamma\frac{\partial}{\partial\psi}$ $+\cos\psi\frac{\partial}{\partial\gamma})$	$j_{\lambda y'} =$	$-i$
$j_{\lambda z} =$	$-i\hbar[(\cos\theta+\sin\theta\cos\psi\cot\gamma)\frac{\partial}{\partial\psi}$ $+\sin\theta\sin\psi\frac{\partial}{\partial\gamma}]$	$j_{\lambda Z_\lambda} =$	$-i\hbar\frac{\partial}{\partial\psi}$	$j_{\lambda z'_\lambda} =$	$i\hbar\frac{\partial}{\partial}$
$J^2 =$	$J_x^2+J_y^2+J_z^2$ $=-\hbar^2[\frac{\partial^2}{\partial\theta^2}+cot\theta\frac{\partial}{\partial\theta}+$ $\frac{1}{\sin^2\theta}(\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2}{\partial\psi^2})-\frac{2\cos\theta}{\sin\theta^2}\frac{\partial^2}{\partial\phi\partial\psi}]$	$J^2 =$	$J_{X_\lambda}^2+J_{Y_\lambda}^2+J_{Z_\lambda}^2$ $-i\hbar\cot J_{Y_\lambda}$	$J^2 =$	$J^2_{x'}$
$j_\lambda^2 =$	$j_\lambda^2=j_{\lambda X_\lambda}^2+j_{\lambda Y_\lambda}^2+j_{\lambda Z_\lambda}^2$ $-\hbar^2(\frac{\partial^2}{\partial\gamma^2}+\cot\gamma\frac{\partial}{\partial\gamma}+\frac{1}{\sin^2_\gamma}\frac{\partial^2}{\partial\psi^2})$	$j_\lambda^2 =$	$j_{\lambda X_\lambda}^2+j_{\lambda Y_\lambda}^2+j_{\lambda Z_\lambda}^2$	$j_\lambda^2 =$	$j^2_{\lambda z}$ $-i$
$j_\lambda J =$	$j_{\lambda z}J_z+j_{\lambda x}Jx+j_{\lambda Y}Jy$	$j_\lambda J =$	$j_{\lambda Z_\lambda}J_{Z_\lambda}+j_{\lambda X_\lambda}J_{X_\lambda}$	$j_\lambda J =$	j_λ

(a) The subscript λ has been omitted from the symbols $\theta, \phi, \gamma, \psi$ The expressions for J^2, j_λ^2 and $j_\lambda J$ in terms of $\theta, \phi, \gamma, \psi$ are independent of coordinate system.

The rotationally coupled Schrödinger equation; tumbling - decoupling approximations

• expansion of the body-fixed wavefunctions $\Psi^{\lambda}_{J\Omega_\lambda}$ in spherical harmonics $Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda,\psi_\lambda)$ (eigenfunctions of $\mathbf{j}^2_\lambda$ and $j_{\lambda z_\lambda}$):

$$\Psi^{\lambda}_{J\Omega_\lambda}(r_\lambda,R_\lambda,\gamma_\lambda,\psi_\lambda)=\sum_{j_\lambda=|\Omega_\lambda|}^{\infty}Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda,\psi_\lambda)w^{\lambda}_{Jj_\lambda\Omega_\lambda}(r_\lambda,R_\lambda),$$

$$\Omega_\lambda=-J...+J, J=0,1,2,... \qquad (179)$$

• substitute this into 175, multiply throughout by $Y^*_{j'_\lambda\Omega'_\lambda}(\gamma_\lambda,\psi_\lambda)$ and integrate over γ_λ and ψ_λ (volume element $\sin\gamma_\lambda d\gamma_\lambda d\psi_\lambda$) finally interchange the primed

and unprimed quantum numbers, a SE in the two scaled distances r_λ, R_λ:

$$(t^{J\lambda j_\lambda}_{\Omega_\lambda\Omega_\lambda} - E)w^\lambda_{Jj_\lambda\Omega_\lambda}(r_\lambda, R_\lambda) + \sum_{j'_\lambda=|\Omega_\lambda|}^{\infty} V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda} w^\lambda_{Jj'_\lambda\Omega_\lambda}(r_\lambda, R_\lambda) +$$

$$t^{J\lambda j_\lambda}_{\Omega'_\lambda\Omega_\lambda+1} w^\lambda_{Jj_{\lambda'}\Omega_\lambda+1i}(r_\lambda, R_\lambda) + t^{J\lambda j_\lambda}_{\Omega_\lambda-1} w^\lambda_{Jj_{\lambda'}\Omega_\lambda-1}(r_\lambda, R_\lambda) = 0 \qquad (180)$$

$$J = 0, 1, 2...; \;\; \Omega_\lambda = -J, .. + J; \;\; j_\lambda = |\Omega_\lambda|, |\Omega_\lambda| + 1, ...$$

$$t^{J\lambda j_\lambda}_{\Omega_\lambda\Omega_\lambda} = -\frac{\hbar}{2\mu}(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R^2_\lambda}R_\lambda + \frac{1}{r_\lambda}\frac{\partial^2}{\partial r^2_\lambda}r_\lambda) + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r^2_\lambda} +$$

$$\frac{\hbar^2}{2\mu R^2_\lambda}[J(J+1) - 2\Omega^2_\lambda + j_\lambda(j_\lambda+1)] \qquad (181)$$

$$t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda\pm1} = -\frac{\hbar^2}{2\mu R_\lambda^2}\xi_\pm(J,\Omega_\lambda)\xi_\pm(j_\Omega,\Omega_\lambda) \tag{182}$$

$$\xi_\pm((J,\Omega_\lambda) = [J(J+1) - \Omega_\lambda(\Omega_\lambda \pm 1)]^{1/2}, |\Omega_\lambda| \leq J \tag{183}$$

$$V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda}(r_\lambda, R_\lambda) = \langle j_\lambda\Omega_\lambda|V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)|j'\Omega_\lambda\rangle \tag{184}$$

- for systems confined to a space-fixed plane Ω_λ does not appear (or it can be considered to have the fixed value zero) since the system does not tumble, and there is therefore no Ω_λ coupling

- in that case, j_λ assumes all integer values, including negative ones, and there is one set of j_λ coupled equations for each J

- in the present three-dimensional case there is both j_λ and Ω_λ coupling, but still no J coupling

• kinetic energy matrix $\mathbf{t}^{j\lambda}(r_\lambda, R_\lambda)$ (which includes the centrifugal potential terms) and a potential energy matrix $\mathbf{V}^{\lambda}(r_\lambda, R_\lambda)$ whose rows and columns are scanned by the indices $j_\lambda, \Omega_\lambda$ and $j'_\lambda, \Omega'_\lambda$:

$$(\mathbf{t}^{J\lambda})^{j'_\lambda \Omega'_\lambda}_{j_\lambda \Omega_\lambda} = \delta_{j_\lambda j'_\lambda} \sum_{i=-1}^{1} \delta_{\Omega_\lambda \Omega'_{\lambda - i}} t^{J\lambda j_\lambda}_{\Omega'_\lambda \; \Omega_\lambda + i} \tag{185}$$

$$(\mathbf{V}^{\lambda})^{j'_\lambda \Omega'_\lambda}_{j_\lambda \Omega_\lambda} = \delta_{\Omega_\lambda \Omega'_\lambda} V^{\lambda \Omega}_{j_\lambda j'_\lambda} \tag{186}$$

$\mathbf{t}^{J\lambda}$ is diagonal in j_λ (and tridiagonal in Ω_λ), $\mathbf{V}^{\lambda}$ is diagonal in Ω_λ

• defining $w^\lambda_J(r_\lambda, R_\lambda)$ as the column vector whose elements, scanned by $j_\lambda, \Omega_\lambda$ are the functions $w^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda)$ 180 can be rewritten as

$$(\mathbf{t}^{J\lambda} + \mathbf{V}^{\lambda}) w^\lambda_J = E w^\lambda_j \tag{187}$$

- 187 shows clearly that the potential coupling is diagonal in Ω_λ

- this, along with the weakness of the centrifugal coupling (due to the terms in $\mathbf{t}^{J\lambda}$ of angular origin) for small J and j_λ has lead to the development of fairly accurate tumbling-decoupling approximations by several workers in studies of non-reactive atom-diatom scattering

- in such procedures, the $t^{J\lambda j}_{\Omega_\lambda,\Omega_\lambda\pm1}$ terms in 180 and 185 are neglected, thereby making 187 be diagonal in Ω_λ

- in addition, the $\hbar^2/2\mu R_\lambda^2$ term in 181 [which arises from the l_λ^2 term in 170] is usually replaced by an approximate expression

.- Pack replaces it by $\hbar^2 J(J+1)/2\mu R_\lambda^2$ and McGuire and Kouri by $\hbar^2 l_\lambda(l_\lambda+1)/2\mu R_\lambda^2$, with l_λ in space-fixed system

- reactive scattering: an Ω_λ decoupling requires neglect of the $t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_{\lambda\pm1}}$ in 180

for each arrangement channel region $\lambda = \alpha, \beta, \gamma$

- the potential coupling matrix of 184 and (2.26) may be conveniently calculated by expanding the potential $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ in a series of Legendre polynomials

$$V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) = \sum_{k=0}^{\infty} V_k^\lambda(r_\lambda, R_\lambda) P_k(\cos\gamma_\lambda) \tag{188}$$

substituted into 184:

$$V_{j_\lambda j'_\lambda}^{j\Omega_\lambda}(r_\lambda, R_\lambda) = \sum_{k=0}^{\infty} \left(\frac{2j_\lambda + 1}{2j'_\lambda + 1}\right)^{1/2} C(j_\lambda k j'_\lambda; \Omega_\lambda 0 \Omega_\lambda) C(j_\lambda k j'_\lambda; 000) V_k^\lambda(r_\lambda, R_\lambda) \tag{189}$$

C: Clebsch-Gordan coefficients

- for collisions of an atom with a homonuclear diatomic molecule (as in H + H_2),

the only nonzero terms in 188 occur for even k [since $V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda)$ is symmetric about $\gamma_\lambda = \pi/2$]

$$C(j_k k j'_\lambda; 000) = 0 \quad \text{for } j_\lambda + k + j'_\lambda = \text{odd} \tag{190}$$

$\mathbf{V}^\lambda$ does not couple even with odd rotational states

189 involves a single sum over products of Clebsch-Gordan coefficients, a substantial simplification over the corresponding space-fixed expansion which requires 6-j symbols

define a new function $F^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda)$:

$$F^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda) = R_\lambda r_\lambda w^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda) \tag{191}$$

substitution into 180:

$$(\bar{t}^{J\lambda j_\lambda}_{\Omega_\lambda\Omega_\lambda} - E)F^\lambda_{Jj_\lambda\Omega_\lambda} + \sum_{j'_\lambda} V^{\lambda\Omega_\lambda}_{j_\lambda j'_\lambda} F^\lambda_{Jj'_\lambda\Omega_\lambda} + t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda+1} F^\lambda_{Jj'_\lambda\Omega_\lambda+1} + t^{J\lambda j_\lambda}_{\Omega_\lambda,\Omega_\lambda-1} F^\lambda_{Jj'_\lambda\Omega_\lambda-1} = 0 \tag{192}$$

$$\bar{t}^{J\lambda j_\lambda}_{\Omega_\lambda\Omega_\lambda} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial R^2_\lambda}\right) + \frac{\partial^2}{\partial r^2_\lambda} + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r^2_\lambda} + \frac{\hbar^2}{2\mu R^2_\lambda}[J(J+1) - 2\Omega^2_\lambda + j_\lambda(j_\lambda+)] \tag{193}$$

in matrix form:

$$(\bar{\mathbf{t}}^{J\lambda} + \mathbf{V}^\lambda)\mathbf{F}^\lambda_j = E\mathbf{F}^\lambda_j \tag{194}$$

$\bar{t}^{J\lambda}$ is defined similarly to $t^{J\lambda}$ and F^λ_J similarly to w^λ_J

- 192 and 194 are called the body-fixed rotationally coupled SE

Angular momentum operators and the Schrödinger equation in space-fixed and body-fixed coordinate systems

Relations between the rotational and total angular momentum operators in the space-fixed and body-fixed coordinate systems

- space-fixed coordinate system Oxyz:

in terms of the variables $\phi_{r_\lambda}, \theta_{r_\lambda}, \phi_\lambda$ and θ_λ, components of $(\mathbf{j}_\lambda)$

$$j_{\lambda z} = -i\hbar \frac{\partial}{\partial \phi_{r_\lambda}} \tag{195}$$

$$j_{\lambda x} = -i\hbar(-\cos\phi_{r_\lambda} \cot\theta_{r_\lambda} \frac{\partial}{\partial \phi_{r_\lambda}} - \sin\phi_{r_\lambda} \frac{\partial}{\partial \theta_{r_\lambda}}) \tag{196}$$

$$j_{\lambda y} = -i\hbar(\sin\phi_{r_\lambda}\cot\theta_{r_\lambda}\frac{\partial}{\partial\phi_{r_\lambda}} + \cos\phi_{r_\lambda}\frac{\partial}{\partial\theta_{r_\lambda}}) \tag{197}$$

similar expressions for the components of $\mathbf{l}_\lambda$ with $\phi_\lambda, \theta_\lambda$ substituted for $\phi_{r_\lambda}, \theta_{r_\lambda}$

components of $\mathbf{J}$: $\mathbf{J} = \mathbf{l}_\lambda + \mathbf{j}_\lambda$

- the eigenfunctions j_λ^2 and l_λ^2 in 170 (and also of $j_{\lambda z}$ and $l_{\lambda z}$) are the spherical harmonics $Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda}), \phi_{r_\lambda}$ and $Y_{l_\lambda m_{l_\lambda}}(\theta_\lambda, \phi_\lambda)$

modified associated Legendre function $\mathcal{P}_j^{m_j}$:

$$\mathcal{P}_j^{m_j}(\cos\theta) = P_j^{|m_j|}(\cos\theta)(\frac{(j-|m_j|)!}{j+|m_j|)!}\frac{2j+1}{2})^{1/2} \times \begin{cases}(-1)^{m_j} & m_j > 0\\ 1 & m_j \leq 0\end{cases} \tag{198}$$

$P_j^{|m_j|}$: associated Legendre function

spherical harmonic Y_{jm_j}:

$$Y_{jm_j}(\theta,\phi) = \frac{e^{im_j\phi}}{\sqrt{2\pi}}\mathcal{P}_j^{m_j}(\cos\theta) \tag{199}$$

space-fixed formalism of Arthurs and Dalgarno:

full wavefunction is expanded in terms of a set of functions $\mathcal{Y}_{l_\lambda j_\lambda}^{JM}(\theta_\lambda,\phi_\lambda;\theta_{r_\lambda},\phi_{r_\lambda})$, which are simultaneous eigenfunctions of J^2, J_z, l_λ^2 and j_λ^2

$\mathcal{Y}_{l_\lambda j_\lambda}^{JM}$ are related to the $Y_{j_\lambda,m_{j_\lambda}}$ and $Y_{l_\lambda}m_{l_\lambda}$ via

$$\mathcal{Y}_{l_\lambda j_\lambda}^{JM}(\theta_\lambda,\phi_\lambda;\theta_{r_\lambda},\phi_{r_\lambda}) = \sum_{m_{j_\lambda},m_{l_\lambda}} C(j_\lambda l_\lambda J; m_{j_\lambda} m_{l_\lambda} M)\times Y_{j_\lambda m_{j_\lambda}}(\theta_{r_\lambda},\phi_{r_\lambda})Y_{l_\lambda m_{l_\lambda}}(\theta_\lambda,\phi_\lambda) \tag{200}$$

full space-fixed wavefunction:

$$\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{l_\lambda j_\lambda} \mathcal{Y}^{JM}_{l_\lambda j_\lambda}(\theta_\lambda, \phi_\lambda; \theta_{r_\lambda}, \phi_{r_\lambda}) G^{JM}_{j_\lambda l_\lambda}(r_\lambda, R_\lambda) \tag{201}$$

space-fixed coupled SE for $G^{JM}_{j_\lambda l_\lambda}$:

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda + \frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda\right) + \frac{j_\lambda(j_\lambda+1)\hbar^2}{2\mu r_\lambda^2} + \frac{l_\lambda(l_\lambda+1)\hbar^2}{2\mu R_\lambda^2} - E\Big] G^{JM}_{j_\lambda l_\lambda} + \sum_{j'_\lambda l'_\lambda} \langle l_\lambda j_\lambda | V | l'_\lambda j'_\lambda \rangle G^{JM}_{j_\lambda l_\lambda} = 0 \tag{202}$$

Transformation to the body-fixed coordinate systems $OX_\lambda Y_\lambda Z_\lambda$ and $Ox'_\lambda y' z'_\lambda$:

• a convenient representation of angular momentum operators in these coordinate systems involves choosing the operators **J** and $\mathbf{j}_\lambda$ as independent and expressing the l_λ^2 of 170 by the expansion:

$$l_\lambda^2 = |J - j_\lambda|^2 = J^2 j_\lambda^2 - (J j_\lambda + j J_\lambda) \tag{203}$$

• to convert the operators j_λ and J, and thus the Hamiltonian of 170 to the body-fixed systems requires first a change from the variables $\theta_\lambda, \phi_\lambda, \theta_{r_\lambda} \phi_{r_\lambda}$ to $\theta_\lambda, \phi_\lambda, \gamma_\lambda, \psi_\lambda$, followed by successive rotations of the components of the operators

• rotational transformations: using the general expression

$$J_{k'} = R(\alpha\beta\gamma)^{-1} J_k R(\alpha\beta\gamma) \tag{204}$$

J_k: kth component of J in an initial system and

$$R(\alpha\beta\gamma) = e^{i\gamma J_z/\hbar} e^{i\beta J_y/\hbar} e^{i\alpha J_z/\hbar} \tag{205}$$

$J_{k'}$: k' component of $\mathbf{J}$ in a transformed coordinate system, which is obtained through rotations by Euler angles $\alpha\beta\gamma$ from the initial system

see Table 1 for the resulting components of the operators J and j_λ

in terms of the coordinate system $OX_\lambda Y_\lambda Z_\lambda$ the Hamiltonian of 170is :

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2} R_\lambda + \frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2} r_\lambda\right) + \frac{j_\lambda^2}{2\mu r_\lambda^2} +$$

$$\frac{1}{2\mu R_\lambda^2}[J^2 + {}^2_\lambda - 2j_{\lambda z_\lambda} J_{Z_\lambda} - (j_\lambda^- J^+ + j_\lambda^+ J^-)] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) \tag{206}$$

• in order to express the SE in $OX_\lambda Y_\lambda Z_\lambda$ coordinates, the wavefunction is rotated according to 174; substituting this expression, along with 206 into 170, and using

$$J^{\pm} D^J_{M\Omega_\lambda} = \hbar[J(J+1) - \Omega_\lambda(\Omega_\lambda \mp 1)]^{1/2} D^J_{M\Omega_\lambda \mp 1}, \tag{207}$$

($\pm$: components refer to the body-fixed system)

coupled equations for the $\Psi^{\lambda}_{J\Omega_\lambda}$:

$$
\begin{aligned}
&- [\frac{\hbar}{2\mu}(\frac{1}{R_\lambda}\frac{\partial^2}{\partial R_\lambda^2}R_\lambda + \frac{1}{r_\lambda}\frac{\partial^2}{\partial r_\lambda^2}r_\lambda) + \frac{j_\lambda^2}{2\mu r_\lambda^2} + \\
&\frac{1}{2\mu R_\lambda^2}[J(J+1)\hbar^2 + j_\lambda^2 - 2\hbar\Omega_\lambda j_{\lambda z_\lambda}] + V^\lambda(r_\lambda, R_\lambda, \gamma_\lambda) - E]\Psi^{\lambda}_{J\Omega_\lambda} \\
&-\frac{\hbar}{2\mu R_\lambda^2}[J(J+1) - \Omega_\lambda(\Omega_\lambda+1)]^{1/2} j_\lambda^- \Psi^{\lambda}_{J,\Omega_\lambda+1} - \\
&\frac{\hbar}{2\mu R_\lambda^2}[J(J+1) - \Omega_\lambda(\Omega_\lambda-1)]^{1/2} j_\lambda^+ \Psi^{\lambda}_{J,\Omega_\lambda-1} = 0 \qquad (208)
\end{aligned}
$$

$Y_{j_\lambda\Omega_\lambda}(\gamma_\lambda, \psi_\lambda)$: rotational eigenfunctions in $OX_\lambda Y_\lambda Z_\lambda$

- rotationally coupled body-fixed solutions analogous to 201

$$\Psi_{JM}(\mathbf{r}_\lambda, \mathbf{R}_\lambda) = \sum_{j_\lambda, \Omega_\lambda} D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0) Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) w^\lambda_{J j_\lambda \Omega_\lambda}(r_\lambda, R_\lambda) \qquad (209)$$

(combination of 179 and 174)

- the body-fixed and space-fixed representations are related :

$$D^J_{M\Omega_\lambda}(\phi_\lambda, \theta_\lambda, 0) Y_{j_\lambda \Omega_\lambda}(\gamma_\lambda, \psi_\lambda) =$$

$$(\frac{4\pi}{2J+1})^{1/2} \sum_{l_\lambda} (-1)^{j_\lambda - \Omega_\lambda} C(J j_\lambda l_\lambda; \Omega_\lambda - \Omega_\lambda 0) \mathcal{Y}^{JM}_{j_\lambda l_\lambda}(\theta_\lambda, \phi_\lambda; \theta_{r_\lambda} \phi_{r_\lambda}) \qquad (210)$$

- 210 is of great utility in the asymptotic analysis

References

[1] M. Baer, ed., Theory of Chemical Reaction Dynamics, Vols. I-IV, CRC Press, Boca Raton, FL, 1985.

[2] D. C. Clary, ed., The Theory of Chemical Dynamics, Dordrecht: Reidel 1986.

[3] W. H. Miller, ed., Dynamics of Molecular Collisions, Parts A and B (Vols. 1 and 2 of Modern theoretical Chemistry), Plenum, NY, 1976.

[4] J. M. Bowman, ed., Advances in Molecular Vibrations and Collision Dynamics, Vol. 2, JAI Press, Greenwich, CT, 1994.

[5] R. B. Bernstein, ed., Atom-Molecule Collision Theory: a Guide for the Experimentalist, Plenum, NY, 1979.

[6] J. Z. H. Zhang and R. E. Wyatt, Eds., Dynamics of molecules and chemical reactions, Dekker (1996)

[7] Tsipis et al, Eds., New methods in quantum theory, NATO, Series 3, Vol. 8, 1997

[8] C. Cerjan, Ed., Numerical Grid Methods and their Application to Schrödinger's Equation, NATO ASI Series C 412 (Kluwer, Dordrecht, 1993)

[9] Supercomputer algorithms for reactivity, dynamics and kinetics of small molecules, Ed. A. Lagana, Kluwer, Dordrecht, 1989.

[10] W. H. Miller, in NATO book 1995, Ed. Yurtsever

[11] F. Mrugala, Int. Rev. Phys. Chem., 12 (1993) 1

[12] D. J. Kouri and D. K. Hoffman, in 'Multiparticle quantum scattering with applications to nuclear, atomic and molecular physics', Eds. D. G. Tuhlar, B. Simon, Springer 1997

[13] D. E. Manolopoulos and D. C. Clary, Ann. Rep. C Roy. Soc. of Chem. 80, 95 (1989).

[14] KUPPERMANN, A., 1981, Theoretical Chemistry and Perspectives, 6A, edited by D. Henderson (New York: Academic), p. 79.

[15] Schatz, G. C., and Kupperman, A. (1976). J. Chem. Phys. 65, 4642-4667.

[16] J. M. Launay in Dynamical Processes in Molecular Physics (Institute of Physiscs Publishing Bristol and Philadelphia, ed. G. Delgado-Barrio) (1991) 97

[17] R. D. Levine, R. B. Bernstein, Molecular Reaction Dynamics, Oxford, 1974.

[18] D. Secrest, in [5]

[19] D. Truhlar, Muckerman, in [5]

[20] D. Micha, Adv. Chem. Phys. **30**, 7, 1975.

[21] KOURI, D. J., and BAER, M., 1986, The Theory of Chemical Dynamics, edited by D. C. Clary (Dordrecht: Reidel), p. 359.

[22] MARCUS, R. A., 1966, J. Chem. Phys., 45, 4493, 4500

[23] LIGHT, J. C., 1971, Methods in Computational Physics, 10, edited by B. Alder, S. Fernbach and M. Rotenberg (New York: Academic), p. 111.

[24] SMITH, F. T., 1960, Phys. Rev., 118, 349

[25] SMITH, F. T., 1960, Phys. Rev., 120, 1058; 1969, Ibid., 179, 111.

[26] JOHNSON, B. R., 1973, J. Comput. Phys., 13, 445; 1978a, J. Chem. Phys., 67, 4086; 1978b, Ibid., 69, 4678; 1980, Ibid., 73, 5051.

[27] WALKER, R. B., and LIGHT, J. C., 1980, Ann. Rev. Phys. Chem., 31, 401.

[28] BAER, M., 1982, Adv. Chem. Phys., edited by 1. Prigogine and S. A. Rice (New York: Wiley), Vol. 49, p. 191 ; 1989, Phys. Rep., 178, 99.

[29] BASILEVSKY, M. V., and RYABOY, V. M., 1982, Adv. quant. Chem., edited by P. 0. Löwdin (New York: Academic), Vol. 15, p. 1.

[30] ZHANG, J. Z. H., and MILLER, W. H., 1987, Chem. Phys. Lett., 140, 329.

[31] ZHANG, J. Z. H., and MILLER, W. H., 1989, J. Chem. Phys., 91, 1528; 1990, Ibid., 92, 1811.

[32] LINDERBERG, J., PADKJAER, S. B., ÖHRN, Y., and VESSAL, B., 1989, J. Chem. Phys., 90, 6254.

[33] SCHWENKE, D. W., HAUG, K., ZHAO, M., TRUHLAR, D. G., SUN, Y., and KOURI, D. J., 1988, J. Phys. Chem., 92, 3202.

[34] ZHANG, J. Z. H., KOURI, D. J., HAUG, K., SCHWENKE, D. W., SHIMA, Y., and TRUHLAR, D. G., 1988, J. Chem. Phys., 88, 2492.

[35] SCHWENKE, D. W., MLADENOVIC, M., ZHAO, M., TRUHLAR, D. G., SUN, Y., and KOURI, D. J., 1989, Supercomputer Algorithms for Reactivity, Dynamics and Kinetics of Small Molecules, edited by A. Lagana (Dordrecht: Kluwer), p. 131.

[36] SUN, Y., KOURI, D. J., TRUHLAR, D. G., and SCHWENKE, D. W., 1990, Phys. Rev. A, 41, 4837.

[37] SUN, Y., KOURI, D. J., and TRUHLAR, D. G., 1990, Nucl. Phys. A, 508, 410.

[38] LESTER, W. A. JR., 1971, Methods in Computational Physics, 10, edited by B. Adler, S. Fernbach and M. Rotenberg (New York: Academic); 1976, Dynamics of Molecular Collisions, Part, A, edited by W. H. Miller (New York: Plenum), p. 1.

[39] WYATT, R. E. 3 1979, Atom-Molecule Collision Theory. A Guide for the Experimentalists, edited by R. B. Bernstein (New York: Plenum), p. 477.

[40] SCHATZ, G. C., 1986, The Theory of Chemical Dynamics, edited by D. C. Clary (Dordrecht: Reidel), p. 1; 198 8, Chem. Phys. Lett., 150, 92; 1989, J. Chem. Phys., 90, 3582.

[41] Pack R T and Parker G A 1987 J. Chem. Phys., 87, 3888 Quantum reactive scattering in three dimensions using hyperspherical coordinates : Theory

[42] PACK, R. T., and PARKER, G. A., 1989, J. Chem. Phys., 90, 3511.

[43] PARKER, G. A., PACK, R. T., ARCHER, B. J., and WALKER, R. B., 1987, Chem. Phys. Lett., 137, 564.

[44] BACIC, Z., KRESS, J. D., PARKER, G. A., and PACK, R. T., 1990, J. Chem. Phys., 92, 2344.

[45] DARAKJIAN, Z., HAYES, E. F., PARKER, G. A., BUTCHER, E. A., and KRESS, J. D., 1991, J. Chem. Phys., 95, 2516.

[46] ELKOWITZ, A. B ., and WYATT, R. E., 1975, J. Chem. Phys., 63, 702.

[47] SCHATZ, G. C., and KUPPERMANN, A., 1976, J. Chem. Phys., 65, 4642.

[48] WALKER, R. B., LIGHT, J. C., and ALTENBERGER-SICZEK, A., 1976, J. Chem. Phys., 64, 1166.

[49] LIGHT, J. C., and WALKER, R. B., 1976a, J. Chem. Phys., 63, 1598; 1976b, Ibid., 65, 4272.

[50] KUPPERMANN, A., KAYE, J. A., and DWYER, J. P. , 1980, Chem. Phys. Lett., 74, 257.

[51] KUPPERMANN, A., and HIPES, P. G., 1986, J. Chem. Phys., 84, 5962.

[52] CUCCARO, S. A., HIPES, P. G., and KUPPERMANN, A. , 1989, Chem. Phys. Lett., 154, 155.

[53] HAUKE, G., MANZ, J., and RÖMELT, J., 1980, J. Chem. Phys., 73, 5040.

[54] RÖMELT, J., 1980, Chem. Phys. Lett., 74, 263; Ibid., 87, 259.

[55] DIESTLER, D. J ., 1971, J. Chem. Phys., 54, 4547.

[56] STECHEL, E. B., SCHMALZ, T. G., and LIGHT, J. C., 1979, J. Chem. Phys., 70, 5640.

[57] Top, Z. H., and SHAPIRO, M., 1983, J. Chem. Phys., 77, 5009.

[58] SCHWENKE, D. W., TRUHLAR, D. G., and KOURI, D. J., 1987, J. Chem. Phys., 86, 2772.

[59] SCHATZ, G. C., 1986, The Theory of Chemical Dynamics, edited by D. C. Clary (Dordrecht: Reidel), p. 1; 1988, Chem. Phys. Lett., 150, 92; 1989, J. Chem. Phys., 90, 3582.

[60] Y. T. Lee, et al., J. Chem. Phys. 53, 2123 (1970); 53, 3755 (1970); 55, 5762 (197 1); 56, 1511 (1972); 56, 5801 (1972); 59, 601 (1973).

[61] R. B. Bernstein, Adv. Chem. Phys. 10, 75 (1966).

[62] K. W. Ford and J. A. Wheeler, Ann. Phys. 7, 259, 287 (1959).

[63] M. V. Berry and K. E. Mount, Rept. Prog. Phys. 35, 315 (1972).

[64] (a) M. S. Child, Semiclassical Mechanics with Molecular Applications, Oxford U. P., 1991. (b) W. H. Miller, Science 233, 171 (1986).

[65] (a) P. A. Robinson and R. A. Holbrook, Unimolecular Reactions, Wiley, NY, 1972. (b) W. Forst, Theory of Unimolecular Reactions, Academic Press, NY, 197 3. (c) R. G. Gilbert and S. C. Smith, Theory of Unimolecular and Recombination Reactions, Blackwell, Oxford, 1990.

[66] E. g., see J. Troe, J. Chem. Phys. 97, 288 (1992), and references therein.

[67] (a) W. A. Lester, ref. [3], p. 1. (b) J. C. Light, ref. [5], p. 239. (c) See, e. g., D. Secrest, in ref. [5], pp. 265, 377.

[68] (a) R. N. Porter and L. M. Raff, ref. [3], pg. 1. (b) W. H. Hase, ref. [3], p. 121. (c) M. D. Pattengill, ref. [5], p. 359. (d) L. M. Raff and D. L. Thompson, ref. [1], vol. 111, p. 2.

[69] . E. g., (a) D. A. Micha, ref. [3], p. 81. (b) H. K. Shin, ref. [3], p. 131. (c) R. E. Wyatt, ref. [5], p. 477. (d) J. Jellinek and D. J. Kouri, ref. [1], Vol. II, p. 1.

[70] W. H. Miller, Adv. Chem. Phys. 25, 69 (1974); 30, 77 (1975).

[71] W. H. Miller, Ann. Rev. Phys. Chem. 41, 245 (1990).

[72] W. A. Lester, in [3], p. 1.

[73] J. C. Light, in [5], p. 239.

[74] D. Secrest, in [5], pp. 265, 377.

[75] MILLER, W. H., 1969, J. Chem. Phys., 50, 407.

[76] Burke Taylor 1966

[77] Tang Mehre Thompson 1978

[78] G. Wolken and M. Karplus, J. Chem. Phys. 60, 351 (1974).
Soc. of Chem. 80, 95 (1989).

[79] A. Kuppermann, in ref. [4], and earlier references therein.

[80] W. H. Miller and B. M. D. D. Jansen op de Haar, J. Chem. Phys. 86, 6213 (1987).

[81] J. Z. H. Zhang, S. I. Chu, and W. H. Miller, J. Chem. Phys. 88, 6233 (1988).

[82] J. Z. H. Zhang and W. H. Miller, J. Chem. Phys. 91, 1528 (1989).

[83] . (a) D. G. Truhlar and D. J. Kouri, et al., J. Chem. Phys. 91, 1643 (1989). (b) D. G. Truhlar and D. J. Kouri, et al., J. Phys. Chem. 92, 3202 (1988).

[84] D. E. Manolopoulos and R. E. Wyatt, Chem. Phys. Lett. 152, 23 (1988); 159, 123 (1989); J. Chem. Phys. 91, 6096 (1989); 93, 403 (1990).

[85] S. L. Mielke, D. G. Truhlar, and D. W. Schwenke, J. Phys. Chem. 98, 1053 (1994).

[86] J. M. Launay and M. Le Dournef, Chem. Phys. Lett. 169, 473 (1990).

[87] R. T Pack, E. A. Butcher, and G. A. Parker, J. Chem. Phys. 99, 9310 (1993).

[88] W. H. Miller, Accts. Chem. Res. 26, 174 (1993).

[89] (a) W. H. Miller, S. D. Schwartz, and J. W. Tromp, J. Chem. Phys. 79, 4889 (1983). (b) T. Seideman and W. H. Miller, J. Chem. Phys. 96, 4412 (1992); 97, 2499 (1992).

[90] U. Manthe and W. H. Miller, J. Chem. Phys. 99, 3411 (1993).

[91] D. Thirumalai, B. C. Garrett, and B. J. Berne, J. Chem. Phys. 83, 2972 (1985).

[92] V. A. Mandelshtam and H. S. Taylor, J. Chem. Phys. 99, 222 (1993).

[93] (a) M. Baer and C. Y. Ng, eds., Advances in Chemical Physics, 82, Part 2, 1992. (b) M. S. Child, in ref. [5], p. 427.

[94] Extensive references and many recent papers describing computational methods for the TDSE can be found in Time-Dependent Quantum Molecular Dynamics, eds. J. Broeckhove and L. Lathouwers, NATO ASI Series B: Physics Vol. 299 (Plenum, New York, 1992) and in the thematic volume of Compute7 Physics Communications, Ed. K. Kulander, Vol. 63 (North-Holland, Amsterdam, 1991).

[95] R. G. Newton, Scattering Theory of Waves and Particles (Springer-Verlag, New York, 1982).

[96] J. L. Powell and B. Crasemann, Quantum Mechanics (Addison-Wesley, Reading, MA, 1961) pp. 96-98.

[97] The amplitude density for non-reactive scattering was introduced by B. R. Johnson and D. Secrest, J. Math Phys. 7, 2187 (1966) and generalized to reactive scattering by D. J. Kouri, J. Chem. Phys. 51, 5204 (1969). The solution method for the amplitude density was introduced by M. Baer and D. J. Kouri; see, e. g., J. Chem. Phys. 56, 1758 (1972).

[98] D. Secrest, in Atom-Molecule Collision Theory, Ed. R. B. Bernstein (Plenum, New York, 1979) Chp. 8.

[99] J. C. Polany, Angew. Chemie, **99** (1987) 981;
[100] R. M. J. Dantus and A. H. Zewail, J. Chem. Phys., **89** (1988) 6113
[101] R. M. J. Dantus and A. H. Zewail, J. Chem. Phys., **89** (1988) 6128
[102] R. M. J. Dantus and A. H. Zewail, Science, **241** (1988) 1200
[103] A. Kuppermann and G. C. Schatz, J. Chem. Phys., **62** (1975) 2502
[104] G. C. Schatz and A. Kuppermann, Phys. Rev. Lett., **35** (1975) 1266
[105] G. C. Schatz and A. Kuppermann, J. Chem. Phys., **65** (1976) 4642, 4668
[106] R. B. Walker, E. B. Stechel and J. C. Light, J. Chem. Phys., **69** (1978) 2922
[107] J. C. Light and R. B. Walker, J. Chem. Phys., **65** (1967) 4272
[108] F. Webster and J. C. Light, Chem. Phys. Let, **90** (1989) 265, 300
[109] J. Linderberg, J. Int. Quant. Chem., **35** (1989) 801
[110] W. Kohn, Phys. Rev., **74** (1948) 1763
[111] L. Hulthén, Kgl. Fysiogr. Sallsk. Lund Forh., **14** (1944) 21
[112] L. Hulthén, Arkiv. Mat. Ast. Fys., **35A** (1948) 25
[113] T. -Y. Wu and T. Ohmura, Quantum Theory of Scattering (Prentice Hall, Englewood Cliffs, New Jersey, 1962), p. 64
[114] W. H. Miller, Comments At. Mol. Phys., **22** (1988) 115
[115] B. R. Johnson, J. Chem. Phys., **79** (1983) 1906, 1916
[116] C. A. Mead, Chem. Phys., **49** (1980) 23
[117] R. T. Pack, Chem. Phys. Let, **108** (1984) 333
[118] J. M. Launay and B. Lepetit, Chem. Phys. Let, **144** (1988) 346; **151** (1988) 287
[119] K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Z. H. Zhang and D. J. Kouri, J. Phys. Chem., **90** (1986) 6757

[120] K. Haug, D. W. Schwenke, Y. Shima, D. G. Truhlar, J. Z. H. Zhang and D. J. Kouri, J. Phys. Chem., **87** (1987) 1892

[121] J. Z. H. Zhang, D. J. Kouri, K. Haug, D. W. Schwenke, Y. Shima and D. G. Truhlar, J. Phys. Chem., **88** (1988) 2492

[122] D. Kosloff and R. Kosloff, J. Chem. Phys., **52** (1983) 35

[123] D. E. Manolopoulos and R. E. Wyatt, J. Chem. Phys., **92** (1990) 810

[124] J. Z. H. Zhang, Chem. Phys. Lett., **181** (1991) 63

[125] J. M. Launay and M. Le Dourneuf, Chem. Phys. Lett., **169** (1990) 437

[126] G. C. Schatz, Chem. Phys. Lett., **150** (1988) 92

[127] Q. Sun and J. M. Bowman, J. Chem. Phys., **92** (1990) 5201

[128] Q. Sun, D. L. Yang, N. S. Wang and J. M. Bowman, J. Chem. Phys., **93** (1990) 4730

[129] D. Wang and J. M. Bowman, J. Chem. Phys., **96** (1992) 8906

[130] D. C. Clary, Chem. Phys. Lett., **192** (1991) 34 D. C. Clary, J. Chem. Phys., **95** (1991) 7298 D. C. Clary, J. Chem. Phys., **96** (1992) 3656

[131] D. H. Zhang and J. Z. H. Zhang, J. Chem. Phys., **99** (1993) 5615 D. H. Zhang and J. Z. H. Zhang, J. Chem. Phys., **100** (1994) 2697

[132] D. C. Clary and G. C. Schatz, J. Chem. Phys., **99** (1993) 4578

[133] J. Echave and D. C. Clary, J. Chem. Phys., **100** (1994) 3556

[134] J. Z. H. Zhang, S. -I. Chu and W. H. Miller, J. Chem. Phys., **88** (1988) 6233

[135] J. Z. H. Zhang and W. H. Miller, Chem. Phys. Let, **153** (1988) 465

[136] G. C. Groenenboom and D. T. Colbert, J. Chem. Phys., **99** (1993) 9681

[137] J. C. Light, I. P. Hamilton, J. V. Lill, J. Chem. Phys., **84** (1986) 1400

[138] J. Linderberg and B. Vessal, Int. J. Quant. Chem., **31** (1987) 65

[139] A. Kuppermann and P. G. Hipes, J. Chem. Phys., **84** (1986) 5962
[140] P. G. Hipes and A. Kuppermann, Chem. Phys. Let, **133** (1987) 1
[141] R. T. Pack and G. A. Parker, J. Chem. Phys., **87** (1987) 3888
[142] J. Linderberg, S. Padkjaer, Y. Öhrn and B. Vessal, J. Chem. Phys., **90** (1989) 6254
[143] A. Askar, H. Rabitz, J. Chem. Phys., **80** (1984) 3586
[144] R. Jaquet, Comp. Phys. Com., **58** (1990) 275
[145] R. Jaquet, Habilitationsschrift (1987), Siegen (Shaker, Aachen, 1992)
[146] R. Jaquet and U. Schnupf, Chem. Phys., **165** (1992) 287
[147] R. Jaquet and J. Gribkova, Theoret. Chim. Acta, **89** (1994) 363
[148] R. N. Porter and M. Karplus, J. Chem. Phys., **40** (1964) 1105
[149] W. H. Miller, Annu. Rev. Phys. Com., **41** (1990) 245
[150] G. C. Schatz, J. Chem. Phys., **90** (1988) 1237, 4847
[151] M. Baer, ed., Theory of Chemical Reaction Dynamics, Vol 1, CRC Press, Boca Raton, Fl, 1985
[152] Aquilanti in [4]
[153] Clary in [4]
[154] Kuppermann in [6]
[155] R. A. Marcus, J. Chem. Phys. , 45 (1966) 4493
[156] M. S. Child, 'Molecular Collision Theory', Academic Press, London, 1974, chap. 10.
[157] L. M. Delves, Nucl. Phys., 1959, 9, 391; 1960, 20, 275.
[158] F. T. Smith, J. Math. Phys., 1962, 3, 735; R. C. Whitten and F. T. Smith, J. Math. Phys., 1968, 9, 1103; R. C. Whitten, I Math. Phys., 1969, 10, 1631.

[159] A. Kuppermann, Chem. Phys. Lett., 1975, 32, 374.

[160] C. A. Mead, Chem. Phys., 1980, 49, 23; J. Chem. Phys., 1980, 72,3839.

[161] B. R. Johnson, J. Chem. Phys., 1980, 73, 5051; 1983, 79, 1906, 1916.

[162] G. C. Schatz, Chem. Phys. Lett., 1988, 150, 92.

[163] W. H. Miller, J. Chem. Phys., 1969, 50, 407.

[164] M. Baer and D. J. Kouri, Phys. Rev. A, 1971, 4, 1924; J. Chem. Phys., 1972,56, 4840; J. Math. Phys., 1973,14, 1637.

[165] R. Kosloff and D. Kosloff, J. Chem. Phys., 1983, 79, 1823; R. Kosloff, J. Phys. Chem., 1988, 92, 2087.

[166] . N. Brooks and D. C. Clary, J. Chem. Phys., 1990, 92, 4178.

[167] A. Kuppermann and G. C. Schatz, I Chem. Phys., 1975, 62, 2502; 1976, 65, 4642, 4668.

[168] (a) A. B. Elkowitz and R. E. Wyatt, J. Chem. Phys. 62, 2504 (1975i; 62, 3683 (1975); (b) S. A. Harms and R. E. Wyatt, J. Chem. Phys. 62, 3162 (1975); 62, 3173 (1975).

[169] Walker et al 1978

[170] Light Walker 1976, Stechel et al 1978

[171] J. C. Light, R. B. Walker, E. B. Stechel, and T. G. Schmalz, Comp. Phys. Comm, , 1979, 17, 89; J. V. Lill, T. G. Schmalz, and J. C. Light, J. Chem. Phys., 1983, 78, 4456.

[172] R. B. Walker and J. C. Light. Ann. Rev. Phys. Chem., 1980, 31, 401.

[173] E. B. Stechel, F. Webster, and J. C. Light. J. Chem. Phys., 1988, 88, 1824.

[174] F Webster and J. C. Light, J. Chem. Phys., 1989, 90, 265.

[175] F. Webster and J. C. Light, J. Chem. Phys., 1989, 90, 300.

[176] A. Kuppermann in 'Potential Energy Surfaces and Dynamics Calculations', ed. D. G. Truhlar, Plenum Press, New York, 1981, p. 375.

[177] G. A. Parker, R. T. Pack, B. J. Archer, and R. B. Walker, Chem. Phys. Lett., 1987, 137, 564.

[178] G. A. Parker, R. T. Pack, A. Lagani, B. J. Archer, J. D. Kress, and Z. Bacic in 'Supercomputer Algorithms for Reactivity, Dynamics, and Kinetics of Small Molecules', ed. A. Lagana, Kluwer, Dordrecht, 1989, p. 105.

[179] J. D. Kress, Z. Bacic, G. A. Parker, and R. T. Pack, Chem. Phys. Lett., 1989, 157, 484.

[180] J. C. Light, 1. P. Hamilton, and 1. V. Lill, J. Chem. Phys., 1985, 82, 1400.

[181] R. M. Whitnell and J. C. Light, J. Chem. Phys., 1988, 89, 3674.

[182] J. M. Launay and M. Le Dourneuf, Chem. Phys. Lett., 1989, 163, 178.

[183] I-C. Nieh and J. J. Valentini, Phys. Rev. Len., 1988, 60, 519; J. Chem. Phys., 1990, 92, 1083.

[184] J. Z. H. Zhang and W. H. Miller', Chem. Phys. Lett. , 1988, 153, 465.

[185] M. Mishra, J. Linderberg, and Y. Ohm, Chem. Phys. Lett., 1984, 111, 4A

[186] J. Linderberg, Int. J. Quantum Chem. S., 1986, 19, 467.

[187] J. Linderberg and B. Vessal, Int. J. Quantum Chem., 1987, 31, 65.

[188] J. Linderberg, S. B. Padkjaer, Y. ¨Ohrn, and B. Vessal, J. Chem. Phys., 1989, 90, 6254.

[189] A. Kuppermann and P. G. Hipes, J. Chem. Phys., 1986, 94, 5962.

[190] L. Eisenbud, Ph. D. Thesis, Princeton, 1948; E. P. Wigner, Phys. Rev., 1955, 98, 145.

[191] F. T. Smith, Phys. Rev., 1960, 118, 349.

[192] S. A. Cuccaro, P. G. Hipes, and A. Kuppermann, Chem. Phys. Lett., 1989, 154, 155.

[193] G. C. Schatz, Chem. Phys. Lett., 1988, 151, 409.

[194] C. Schatz, J. Chem. Phys., 1989, 90, 3582.

[195] D. W. Schwenke, D. G. Truhlar, and D. J. Kouri, J. Chem. Phys., 1987, 86, 2772.

[196] Y. Öhrn and J. Linderberg, Mol. Phys., 1983, 49, 53,

[197] X. Chapuisat, Chem. Phys. Lett., 1987, 136, 153,

[198] M. Baer, Phys. Rep., 1989, 178, 99.
[199] R. K. Nesbet, 'Variational Methods in Electron- Atom Scattering Theory' Plenum, New 75 York, 1980, chap. 2.
[200] W. Kohn, Phys. Rev., 1948, 74, 1763.
[201] J. Schwinger, Phys. Rev, , 1947, 72, 742.
[202] R. G. Newton, 'Scattering Theory of Particles and Waves', Springer, New York, 1982, p. 320.
[203] C, Schwartz, Phys. Rev., 1961, 124, 1468; Ann. Phys. , New York, 1961, 10, 36.
[204] W. H. Miller and B. M. 13 D. Jansen op de Haar, J. Chem. Phys., 1987, 86, 6213.
[205] A. Messiah, 'Quantum Mechanics', Wiley, New York, 1962, chap. 19.
[206] L. F. X. Gaucher and W. H. Miller, Israel J. Chem., 1989, 29, 349.
[207] R. R. Lucchese, Phys. Rev. A, (1991).
[208] J. Z. H. Zhang, S-I. Chu, and W. H. Miller, J. Chem. Phys., 1988, 88, 6233; 1988, 89, 4454.
[209] W. H. Miller, Collect, Czech. Chem. Commun., 1988, 53, 1873.
[210] W. H. Miller, Comments At. Mol. Phys., 1988, 22, 115.
[211] J. Z. H. Zhang and W. H. Miller, J. Chem. Phys., 1988, 88, 4549; 1989, 90, 7610.
[212] J Z. H. Zhang and W. H. Miller, Chem. Phys. Lett., 1989, 159, 130.
[213] G. C. Schatz, Ann. Rev. Phys. Chem., 1988, 39, 317.
[214] W. H. Miller, Ann. Rev. Phys., Chem., (1991)
[215] Adams, J. T., Smith, R. L., and Hayes, E. F. (1974). J. Chem. Phys. 61, 2193-2199.
[216] Askar, A., Cakmak, A. S., and Rabitz, H. A. (1978). Chem. Phys. 33, 267-286.
[217] Davydov, A. S. (1965). "Quantum Mechanics", Chapter VI. Addison Wesley, Reading, Massachusetts.
[218] Delves, L. M. (1959). Nucl. Phys. 9, 391-399; (1960). Nucl. Phys. 20, 275-308.

[219] Diestler, D. J., and McKoy, V. (1968). J. Chem. Phys. 48, 2951-2959.

[220] Elkowitz, A. B., and Wyatt, R. E. (1975). J. Chem. Phys. 62, 2504-2506.

[221] Elkowitz, A. B., and Wyatt, R. E. (I 975). J. Chem. Phys. 63, 702-72 1.

[222] Eyring, H. (1935). J. Chem. Phys. 3, 107-115.

[223] Gordon, R. G. (1969). J. Chem. Phys. 51, 14-25.

[224] Johnson, B. R. (1972). Chem. Phys. Lett. 13, 172-175.

[225] Kuppermann, A. (1970). In "Proceedings of the Conference on Potential Energy Surfaces in Chemistry" (W. A. Lester, ed.), pp. 121-124. University of California, Santa Cruz.

[226] Kuppermann, A. (1972). Proc. Int. Com. Phys. Electron. At. Collisions, 7th, 1971. pp. 3-5.

[227] Kuppermann, A. (1975). Chem. Phys. Lett. 32, 374-375.

[228] Kuppermann. A., and Schatz. G. C. (1975). J. Chem. Phys. 62, 2502-2504.

[229] Kuppermann, A., Schatz, G. C., and Baer, M. (1976). J. Chem. Phys. 65, 4596-4623.

[230] Lane, A. M., and Thomas, R. G. (1958). Rev. Mod. Phys. 30, 257-353.

[231] Light, J. C., and Walker, R. B. (1976). J. Chem. Phys. 65, 4272-4282.

[232] McCullough, E. A., Jr., and Wyatt, R. E. (1969). J. Chem. Phys. 51, 1253-1254.

[233] McCullough, E. A., Jr., and Wyatt, R. E. (1971). J. Chem. Phys. 54, 3578-3591, 3592-3600.

[234] Miller, G., and Light, J. C. (1971). J. Chem. Phys. 54. 1635-1642, 1643-1651.

[235] Mortensen, E. M. (1968). J. Chem. Phys. 48, 4029-4039.

[236] Mortensen. E. M., and Gucwa, L. D. (1969). J. Chem. Phys. 51, 5695-5702.

[237] Mortensen. E. M., and Pitzer, K. S. (1962). J. Chem. Soc., Spec. Publ. 16, 57-75.

[238] Pack, R, T. (1974). J. Chem. Phys. 60, 633-639.

[239] Rankin, C. C., and Light, J. C. (1969). J. Chem. Phys. 51, 1701-1719.
[240] Sams, W. M., and Kouri, D. J. (1969). J. Chem. Phys. 51, 4809-4814, 4815-4819.
[241] Schatz, G. C., and Kuppermann, A. (1976c). J. Chem. Phys. 65, 4668-4692.
[242] Truhlar, D. G., Kuppermann, A., and Adams, J. T. (1973). J. Chem. Phys. 59, 395-402.
[243] Truhlar, D. G. and Horowitz, C. G. (1978). J. Chem. Phys. 68, 2466-2476.
[244] Truhlar, D. G., and Kuppermann, A. (1970). J. Chem. Phys. 52, 3841-3843.
[245] Truhlar, D. G., and Kuppermann, A. (1972). J. Chem. Phys. 56, 2232-2252.
[246] Walker, R. B., Stechel, E. B. and Light, J. C. (1978). J. Chem. Phys. 69, 2922-2923.
Theory" (R. B. Bernstein, ed.), Chapter 17. Plenum, New York.
[247] L. E. Elsgolc, Calculus of Variations (Pergamon Press, 1961)
[248] J. P. Boyd, Chebyshev and Fourier Spectral Methods (Springer Verlag, New York, 1989)
[249] W. H. Miller und. B. M. D. D. Jansen op de Haar, J. Chem. Phys., **86** (1987) 6213
[250] C. W. McCurdy, T. N. Rescigno, B. I. Schneider, Phys. Rev. A **36** (1987) 2061
[251] C. W. McCurdy, T. N. Rescigno, Phys. Rev. A **37** (1988) 1044
[252] C. W. McCurdy, T. N. Rescigno, B. I. Schneider, Phys. Rev. Lett. **63** (1989) 248
[253] J. E. G. Farina, Quantum Theory of Scattering (Pergamon Press, 1973)
[254] R. K. Nesbet, Variational Methods in Electron-Atom Scattering Theory(Plenum Press, New York 1980)
[255] H. Feshbach, Ann. Phys. (N. Y.) **5** (1958) 357, **19** (1962) 287
[256] A. J. F. Siegert, Phys. Rev. **56** (1939) 750
[257] J. Z. Zhang, W. H. Miller, J. Chem. Phys., **91** (1989) 1528
[258] J. Tennyson, S. Miller, Comp. Phys. Comm., **55** (1989) 149

[259] J. Tennyson, J. R Henderson, J. Chem. Phys., **91** (1989) 3815

[260] B. T. Sutcliffe and J. Tennyson, Mol. Phys., **58** (1986) 1053

[261] H. R. Schwarz, Methode der finiten Elemente, Teubner, Stuttgart, 1988

[262] D. H. Norrie and G. de Vries , The Finite Element Methode, Academic Press, New York, 1973

[263] B. R. Johnson, J. Chem. Phys., **67** (1977) 4086

[264] B. R. Johnson and D. Secrest, J. Math. Phys., **7** (1966) 2187

[265] P. Pechuskas aund J. C. Light, J. Chem. Phys., **44** (1966) 3897

[266] M . Abramowitz and I. A. Stegun, Handbook of Mathematical Functions (National Burreau of Standarts, Washington, D. C. 1968)

[267] M. S. Reeves, M. J. Unekis, D. W. Schwenke, N. M. Harvey, and D. G. Truhlar, RMPROP-Version 2. 1, University of Minnesota, Minneapolis, 1994

[268] W. Eastes, D. Secrest , J. Chem. Phys., **56** (1972) 641

[269] D. G. Truhlar and R. E. Wyatt, Ann. Rev. Phys. Chem., **27** (1976) 1

[270] 1976) H. Eyring and M. Polanyi, Z. Phys. Chem., **B12** (1931) 279 (1977) 45

[271] R. Jaquet, *Theoret. Chim. Acta*, 1987, **71**, 425.

[272] R. Jaquet, *Comp. Phys. Comm.* , 1990, **58**, 257.

[273] J. Z. H. Zhang, S. I. Chu and W. H. Miller, J. Chem. Phys. , 1988, **88**, 6233.

[274] W. H. Miller, *Comments At. Mol. Phys.* , 1988, **22**, 115.

[275] J. Z. H. Zhang and W. H. Miller, Chem. Phys. Let, 1987, **140**, 329.

[276] J. Z. H. Zhang, J. Chem. Phys. , 1991, **94**, 6047.

[277] D. T. Colbert and W. H. Miller, J. Chem. Phys. , 1992, **96**, 1982.

[278] A. K. Belyaev, D. T. Colbert, G. C. Groenenboom and W. H. Miller, Chem. Phys. Let, 1993, **209**, 309.

[279] G. C. Groenenboom and D. T. Colbert, J. Chem. Phys. , 1993, **99**, 9681.

[280] D. H. Zhang and J. Z. H. Zhang, J. Chem. Phys. , 1994, **100**, 2697.

[281] W. H. Miller, in [3], p. 1

[282] L. Hulthén, *Kgl. Fysiogr. Sallsk. Lund Förh.* , 1944, **14**, 21.

[283] L. Hulthén, *Arkiv Mat. Astron. Fysik.* , 1948, **35A**, 25.

[284] W. Kohn, *Phys. Rev.* , 1948, **74**, 1763.

[285] R. K. Nesbet, *Variational Methods in Electron Atom Scattering Theory*, Plenum, New York, 1980.

[286] C. J. Joachain, *Quantum collision theory*, Elsevier, Amsterdam, 1983.

[287] R. N. Porter and M. Karplus, J. Chem. Phys. , 1964, **40**, 1105.

[288] R. Jaquet and J. Gribkova, *Theoret. Chim. Acta*, 1994, **89**, 363.

[289] J. Tennyson and S. Miller, *Comp. Phys. Comm.* , 1989, **55**, 149.

[290] J. Tennyson and J. R Henderson, J. Chem. Phys. , 1989, **91**, 3815.

[291] B. T. Sutcliffe and J. Tennyson, *Mol. Phys.* , 1986, **58**, 1053.

[292] R. Röhse, W. Kutzelnigg, R. Jaquet and W. Klopper J. Chem. Phys. , 1994, **101**, 2231.

[293] J. C. Light, I. P. Hamilton and J. V. Lill. J. Chem. Phys. , 1985, **82**, 1400.

[294] Schatz G C and Kuppermann A 1976 J. Chem. Phys. 65 4642-91 Quantum mechanical reactive scattering for three-dimensional atom plus diatom systems

[295] Elkowitz A B and Wyatt R E 1975 J. Chem. Phys. 62 2504-6 Quantum mechanical reaction cross sections for the three-dimensional hydrogen exchange reaction

[296] Walker R B, Stechel E B and Light J C 1978 J. Chem. Phys. 69 2922-3 Accurate H3 dynamics on an accurate potential surface

[297] Messiah A 1961 Quantum mechanics Vol. 1, Amsterdam: North-Holland Publishing

[298] Arthurs A M and Dalgarno A 1960 Proc. R. Soc. A 256 540-51 The theory of scattering by a rigid rotator

[299] Johnson B R 1983 J. Chem. Phys. 79 1916-25 The quantum dynamics of three particles in hyperspherical coordinates

[300] Johnson B R 1973 J. Comp. Phys. 14 445-9 The multichannel log-derivative method for scattering calculations

[301] Manolopoulos D E 1986 J. Chem. Phys. 85 6425-9 An improved log-derivative method for inelastic scattering

[302] Fock V 1958 D. Kon. Nors. Vidensk. Selsk. Forh. 31 138-52 On the Schrödinger equation of the helium atom

[303] Whitten R C and Smith F T 1968 J. Math. Phys. 9 1103- 13 Symmetric representation for three-body problems. 11 : Motion in space

[304] Kuppermann A 1975 Chem. Phys. Lett. 32 374-5 A useful mapping of triatomic potential energy surfaces

[305] Johnson B R 1980 J. Chem. Phys. 73 5051-8 On hyperspherical coordinates and mapping the internal configurations of a triatomic system

[306] Aquilanti V, Grossi G and Lagana A 1982 J. Chem. Phys. 76 1587-8 On hyperspherical mapping and harmonic expansions for potential energy surfaces Introduction to the quantum theory of reactive scattering 119

[307] Hipes P G and Kuppermann A 1987 Chem. Phys. Letters 133 1-7 Lifetime analysis of high-energy resonances in three-dimensional reactive scattering

[308] Launay J M and Lepetit B 1988 Chem. Phys. Lett. 144 346-352 Three-dimensional quantum study of the reaction H + FH(v, j) $\longrightarrow$ HF(v', j) + H in hyperspherical coordinates

[309] Linderberg J, Padkjaer S, ¨Ohrn Y and Vessal B 1989 J. Chem. Phys. 90 6254-65 Numerical implementation of reactive scattering theory

[310] Launay J M and Le Dourneuf M 1989 Chem. Phys. Lett. 163 178-88 Hyperspherical close-coupling calculation of integral cross sections for the reaction H + H_2 $\longrightarrow$ H_2 + H

[311] Wu Y S M, Cuccaro S A, Hipes P G and Kuppermann A 1991 Theor. Chim. Acta 79 225-39 Quantum chemical reaction dynamics on a highly parallel supercomputer Wu Y S M, Kuppermann A and Lepetit B 1991 Chem. Phys. Lett. 186 319-28 Theoretical calculation of experimentally observable consequences of the geometric phase on chemical reaction cross sections

[312] Pack R T and Parker G A 1989 J. Chem. Phys., 90 3511- 9 Quantum reactive scattering in three dimensions using hyperspherical coordinates : III. Small 9 behaviour and corrigenda

[313] Launay J M and Le Dourneuf M 1990 Chem. Phys. Lett. 169 473-83 Quantum mechanical calculations of integral cross sections for the reaction F + H_2(v=0, j = 0) $\rightarrow$ FH(v', j) + H by the hyperspherical method

[314] Launay J M 1991 Theor. Chim. Acta. 79 183-90 Computation of cross sections for the F + H_2 (v = 0, j = 0) $\rightarrow$ FH(v', j') + H by the hyperspherical method

[315] Launay J M and Padkjaer S B 1991 Chem. Phys. Lett. 181 95-99 Quantum dynamical study of the Cl + H_2 $\rightarrow$ ClH + H reaction

[316] Lepetit B and Launay J M 1991 J. Chem. Phys. 95 5159- 68 Quantum mechanical study of the reaction He + H_2^+ $\rightarrow$ HeH^+ with hyperspherical coordinates

[317] Ed. J. Bowman, Advances in Molecular Vibrations and Collision Dynamics, JAI Press, 1991

[318] S. C. Althorpe et al, J. Chem. Soc., Faraday Trans., 93,703 (1997)

[319] R. Pack in [4]

[320] R. E. Wyatt in [5]

[321] D.E. Manolopolous, J. Chem. Soc., Faraday Trans., 93, 673 (1997)

[322] J. F. Castillo, D. E. Manolopolous, Faraday Discuss. 110, 119, 1998

[323] A. Kuppermann, in [7]

[324] G. Herzberg and H. C. Longuet-Higgins, Intersection of potential energy surfaces in polyatomic molecules, Discussion Faraday Soc. 35: 77 (1963).

[325] H. C. Longuet-Higgins, The intersection of potential energy surfaces in polyatomic molecules, Proc. R. Soc. Lond A 344: 147 (1975).

[326] H. A. Jahn and E. Teller, Stability of polyatomic molecules in degenerate electronic states. 1: Orbital degeneracy, Proc. R. Soc. A 161: 220 (1937).

[327] P. G. Carrick, A. J. Merer, and R. F. Curl, $A^2\Pi \leftarrow X^2\Sigma^+$ infrared electronic transition of C2H, J.Chem. Phys. 78: 3652 (1983).

[328] W. B. Yan, J. L. Hall, J. W. Stephens, M. L. Richnow, and R. F. Curl, Color center laser spectroscopy of excited C_2H, J.Chem Phys. 86: 1657 (1987).

[329] C. Petrongolo, G. Hirsch, and R. J. Buenker, Diabatic representation of theA2A,1h2B, conical intersection in NH2, Mol. Phys. 70: 835 (1990).

[330] G. Hirsch, R. J. Buenker and C. Petrongolo, Ab initio study of NO,. II: Non-adiabatic coupling between the two lowest 2 A' states and the construction of a diabatic representation, Mol. Phys. 70: 835 (1990).

[331] D. C. Robie, M. Hunger, J. L. Bates, and H. Reisler, Product state distributions in the photodissociation of expansion-cooled N02 near the NO(X2n)V = 1 threshold, Chem. Phys. Lett. 193: 413 (1992).

[332] S. P. Walch and R. J. Duchovic, Theoretical characterization of the potential-energy surface for H + 02 - H02* - OH + 0. 111: Computed points to define a global potential-energy surface, J. Chem. Phys. 94: 7068 (1991).

[333] B. Kendrick and R. T. Pack, Potential energy surfaces for the low-lying 2A" and 'A' states of HO,: Use of the diatomics in molecules model to fit ab initio data, J. Chem. Phys. 102: 1994 (1995).

[334] C. A. Mead and D. G. Truhlar, On the determination of Born-Oppenheimer nuclear motion wave functions including complications due to conical intersections and identical nuclei, J. Chem. Phys. 70: 2282 (1979).

[335] Y-S M. Wu, A. Kuppermann and B. Lepetit, Theoretical calculation of experimentally observable consequences of the geometric phase on chemical reaction cross sections, Chem. Phys. Lett. 186: 319 (1991).

[336] Y Aharonov and D. Bohm, Significance of electromagnetic potentials in the quantum theory, Phys. Rev. 115: 485 (1959).

[337] Y-S.M. Wu and A. Kuppermann, Prediction of the effect of the geometric phase on product rotational state distributions and integral cross sections, Chem. Phys. Lett. 201: 178 (1993).

[338] M. V. Berry, Quantal phase factors accompanying adiabatic changes, Proc. R. Soc. Lond. A 392: 45 (1984).

[339] J. W. Zwanziger, M. Koenig, and A. Pines, Berry's phase, Ann. Rev. Phys. Chem. 41: 601 (1990).

[340] G. Schatz et al, Faraday Discuss. 110, 139 (1998)

[341] G. Wolken and M. Karplus, J. Chem. Phys. 60, 351 (1974).

[342] Kuppermann, A. (1975). Chem. Phys. Lett. 32, 374-375.

[343] A. M. Arthurs and A. Dalgarno, Proc. R. Soc. London Ser. A 256, 540 (1960).

[344] . 0. Hirschfelder and E. P. Wigner, Prod. Natl. Acad. Sci. 21, 113 (1935).

[345] C. F. Curtiss, J. 0. Hirschfelder, and F. T. Adler, J. Chem. Phys. 18, 1638 (1950).

[346] R. T. Pack, J. Chem. Phys. 60, 633 (1974).

[347] . S. Davydov, Quantum Mechanics. translated by D. ter Haar.(Addison-Weslay, Reading, MA. 1965), Chap. VI.

[348] P. McGuire and D. J. Kourt, J. Chem. Phys. 60. ?488 (1974).

[349] Handbook of Mathematical Functions, edited by M. Abramowitz and 1. A. Stegun (National Bureau of Standards, Washington. D.C., 1964).

[350] G. C. Schatz and A. Kuppermann, J. Chem. Phys. 65, 4624 (1976).

[351] M. E. Rose, Elementary Theory of Angular Momentum, (Wiley, New York, 1957), Chap. 3.

[352] A. Messiah, Quantum Mechanics, (North-Holland, Amsterdam, 1966), Vol. 11, Eq. X111. 54, p. 530.

[353] D. J. Vezzetti and S. I. Rubinow, Ann. Phys. 35, 373 (1965).

[354] P. M. Morse and H. Feshbach, Methods of Theoretical Physics (McGraw-Hill, New York, 1953), Vol. 11, p. 1721.

[355] A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, Jour. Chem. Phys. 86, 6258 (1987).

[356] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, Jour. Chem. Phys. 95, 4343 (1991).

[357] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, Jour. Chem. Phys. 104, 7139 (1996).

[358] L. Banares, F. J. Aoiz, V. J. Herrero, M. J. D'Mello, B. Niederjohann, K. Seekamp-Rahn, E. Wrede, and L. Schnieder. "Experimental and quantum mechanical study of the H+D2 reaction near 0. 5 eV: The assessment of the H3 potential energy surfaces. " Jour. Chem. Phys. 108, 6160 (1998)

[359] M. P. Miranda, D. C. Clary, J. F. Castillo, and D. E. Manolopoulos. "Using quantum rotational polarization moments to decribe the stereodynamics of the H+D2(v=0, j=0) -¿ HD(v', j')+D reaction. " Jour. Chem. Phys. 108, 3142 (1998)

[360] E. Wrede, L. Schnieder, K. H. Welge, F. J. Aoiz, L. Banares, J. F. Castillo, B. Martinez-Haya, and V. J. Herrero. "The Dynamics of the Hydrogen Exchange Reaction at 2. 20 eV Collision Energy: Comparison of Experimental and Theoretical Differential Cross Sections. " submitted to Jour. Chem. Phys. (1999)

[361] R. Jaquet, A. Kumpf, M. Heinen, J. Chem. Soc., Farad. Trans., **93**, 1027 (1997)

[362] Baer, M., Kouri, D. J., in [2], p. 167.

[363] Jellinek, J., Kouri, D. J., in [1], Vol. 2, Chap. 1.

[364] Ohsaki, A.; Nakamura, H. Phys. Rep. 1990,187, 1.

[365] Bowman, J. M. Adv. Chem. Phys. 1985, 61, 115.

[366] Bowman, J. M.; Wagner, A. F., in [2], p. 47.

[367] Walker, R. B.; Hayes, E. F., in [2], p. 105.

[368] Bowman, J. M. J. Phys. Chem. 1991,95,4960.

[369] Schatz, G. C. In Advances in Molecular Electronic Structure Theory, Dunning, T. H., Jr., Ed.; JAI: Greenwich and London, 1990; Vol. 1, pp. 88-127; Varandas, A. J. C. Adv. Chem. Phys. 1988, 74, 255; Truhlar, D. G.; Steekler, R.; Gordon, M. A. Chem. Rev. 1987,87,217.

[370] A. C. Allison, Adv. At. Mol. Phys., 25, 323 (1988)

Textbooks on Scattering Theory:

N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Clarendon Press, Oxford, 1965), 3rd ed., Chaps. 2-5.

R. G. Newton, Scattering Theory of Waves and Particles (McGraw-Hill, New York, 1966).

L. S. Rodberg and R. M. Thaler, Introduction to the Quantum Theory of Scattering (Academic Press, New York, 1967).

Electronic and Ionic Impact Phenomena, edited by H. S. W. Massey, E. H. S. Burhop, and H. B. Gilbody (Clarendon Press, Oxford, 1969-1974), Vols. 1-5.

M. R. C. McDowell and J. P. Coleman, Introduction to the Theory of Ion-Atom Collisions (North-Holland, Amsterdam, 1970).

M. S. Child, Molecular Collision Theory (Academic Press, New York, 1974).

C. J. Joachain, Quantum Collision Theory (North Holland, Amsterdam, 1975).

L. D. Landau and E. M. Lifshitz, Course of Theo retical Physics (Pergarnon Press, Oxford, 1976), 3rd ed., Vol. 1, Chap. 4, p. 41.

H. Eyring, S. H. Lin, and S. M. Lin, Basic Chemical Kinetics (Wiley, New York, 1980), Chap. 3, p. 81.

B. H. Bransden, Atomic Collision Theory (Benjamin Cummings, Menlo Park, 1983), 2nd ed.

B. H. Bransden and C. J. Joachain, Physics of Atoms and Molecules (Wiley, New York, 1983).

E. E. Nikitin and S. Ya. Umanskil, Theory of Slow Atomic Collisions (Springer-Verlag, Berlin, 1984).

E. W. McDaniel, Atomic Collisions: Electron and Photon Projectiles (Wiley, New York, 1989), Chaps. 3 and 4, p. 71.

M. S. Child, Semiclassical Mechanics with Molecular Applications (Clarendon Press, Oxford, 1991). A. G. Sitenko, Scattering Theory (Springer-Verlag, Berlin, 1991).

E. W. McDaniel, J. B. A. Mitchell, and M. E. Rudd, Atomic Collisions: Heavy Particle Projectiles (Wiley, New York, 1993), Chap. 1, p. 1.